PB-230 428

REMOVAL OF DISSOLVED ORGANIC AND INORGANIC SOLIDS FROM WASTE WATER

Joseph N. J. Cesaro, et al

Syracuse University
Syracuse, New York

September 1965

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REMOVAL OF DISSOLVED ORGANIC AND INORGANIC SOLIDS FROM WASTE WATER

by

Joseph N. J. Cesaro

Allen J. Barduhn

"FINAL REPORT"

Sponsored by

U.S. Public Health Service

Division of Water Supply and Pollution Control

Grant No. WP-00729-01

Syracuse University Account No. 1620.1240

Allen J. Barduhn

Allen J. Barduhn

Principal Investigator

DEPARTMENT OF CHEMICAL ENGINEERING AND METALLURGY

SYRACUSE UNIVERSITY

September 1965

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f = following

I. INTRODUCTION

The system sodium o-dodecylbenzene sulfonate-sodium chloride water (o-NaDBS-NaCℓ-H_2O) was chosen for solubility studies to determine quantitative data concerning the behavior, in the eutectic freezing process, of a dissolved organic material in the presence of a high inorganic salt concentration at low temperatures. In the eutectic process (R-3) for purification of waste water, a major portion of the water is first removed by methods such as evaporation, hydration or freezing. The residue, which contains all the original dissolved organic and inorganic materials, is then exposed to low temperatures at which the ice and inorganic salts precipitate simultaneously. After the eutectic precipitation, it is expected at low temperatures (-10°C) that the high concentration of inorganic salts (23% NaCℓ) in solution would salt out the organic materials.

The NaCℓ was chosen for this study because it is presumed to be the dominant inorganic salt at the eutectic point of sewage. For the organic component of the ternary system, the notorious surfactant found in waste waters NaDBS was selected. It was hoped that the data from this particular ternary system would provide valuable information on the solubility phenomenon in waste water and sewage.

Experimental data on simultaneous solubility of an organic and an inorganic compound at specific temperatures are useful in design of such processes as freezing and hydration when they are concerned with the precipitation of soluble materials from waste water. Also this simultaneous solubility of organic and inorganic salts is of scientific interest for studying such phenomena as the common ion effect. It was expected by

obtaining solubility in the well defined system NaDBS--NaCℓ--H_2O that the salting out behavior or common ion effect would be accurately described.

Sulfonated detergents have risen to prominence because of their low cost of production, excellent detergent and desirable physical properties. Linear alkylate sulfonate (LAS), the straight chain alkylbenzene sulfonate, is a major active ingredient in modern detergents, making up to 20% by weight of the marketed composition. In the past few years, LAS has taken over the surfactant market from ABS (the branched chain, tetrapropylene derived alkylbenzene sulfonate) and in June 1965 emerged as the major surfactant base of the industry. The LAS was substituted for the ABS because of the following reasons:

1. The ABS mixture is resistant to bacterial attack, while the LAS is biodegradable.
2. LAS is considered to be equivalent to the ABS in economy and efficiency of production.
3. LAS has equal or better detergency and foaming properties than ABS.

Commercially prepared alkylbenzene sulfonates are mixtures of ortho, para sulfonate isomers, homologs (variance in carbon number of alkyl chain) and isomers differing in side chain structure. These isomeric side chain structures can be in the form of highly branched alkyl group or random positioning of the phenyl group along a straight carbon chain. Since there is no satisfactory separation technique to resolve such a mixture, it is a problem to obtain a pure form of NaDBS. A requirement for any solubility study is to start with a single pure solute. To conduct this work

successfully, it was necessary to synthesize NaDBS by unequivocal means in the laboratory. This was done only after extensive efforts to purify a relatively pure form of NaDBS (compared to commercial products) failed to alleviate solubility anomalies.

II. LITERATURE SURVEY

Around the year 1916, the Germans first introduced alkylbenzene sulfonates but it was not until the World War II era that international interest intensified in the sulfonate detergent area. For the year 1944, government figures show that synthetic detergent production in the United States reached a total of 350,000,000 pounds (R-12). The use of synthetic detergents in the United States has mushroomed since then and in 1963 synthetic detergent sales were 4 billion pounds (R-10). Unfortunately, their presence in waste waters typifies the contamination of water by modern man.

As of the past few years, there has been considerable interest in the removal of these contaminants from waste water. Stemming from this interest, there have been a number of articles published covering such aspects as their preparation, analytic determination in aqueous solutions, physical and chemical properties. In the following section, a brief resumé of this work is presented.

A. Preparation of Alkylbenzene Sulfonates

Paquette, Lingafelter and Tartar (R-14) presented a comparison of straight chain n-alkylbenzene sulfonates to straight chain aliphatic sulfonates to show the effect of the benzene nucleus on micelle formation. They reported a preparation of the new compounds n-octylbenzene-p-sulfonate and n-dodecylbenzene-p-sulfonate. The preparation consisted of the addition of oleum, at specific conditions, to a purified specie of phenylalkane. Salt formation and extraction then followed.

They reported the solubility of n-octylbenzene-p-sulfonate as 10 gm/l at 25°C and n-dodecylbenzene-p-sulfonate as 2 gm/l at 25°C and 35 gm/l at

60°C. The authors concluded for the two sulfonates (according to Hartley's Theory of Colloidal Electrolytes) that the benzene ring is equivalent to 3-1/2 straight chain carbon atoms for micelle formation.

Gray, Gerecht and Krems (R-5) prepared and sulfonated the following phenylalkanes: 1-phenyloctane, 1-phenyldodecane, 2-phenyltridecane and 5-phenyldodecane. Sulfonation was performed with 20% oleum followed by neutralization with NaOH. The yields for Na-p-octlybenzene sulfonate and Na-p-dodecylbenzene sulfonate were 70% and 80%, respectively. The isomers were identified by derivative formation and infrared spectra.

The ortho isomers of the 1-phenylalkanes were found to be very soluble in water and most organic solvents. The para isomers were found to be insoluble in water and most organic solvents. The authors reported the solubility of p-NaDBS in water as 0.03% at room temperature.

It was concluded that as the phenyl group moves toward the center of a straight carbon chain, the distribution of the ortho isomer decreases, because of steric factors. Furthermore, the para isomer for these alkylbenzenes with the phenyl group located near the center of the straight carbon chain was discovered to be similar in both physical and chemical properties to the ortho isomer, formed from the alkylbenzene with the phenyl group near the end of the chain.

More recently, Gray and Krems (R-6) extended the preparation and sulfonation technique just discussed (R-5) to some other model long chain 1- and 2-phenylalkanes.

B. Analysis of Alkylbenzene Sulfonate Solutions

Weber Morris and Stumm (R-20) carried out ultraviolet absorption

studies on dilute aqueous solutions of alkylbenzene sulfonates. They found that these solutions exhibited a characteristic ultraviolet absorbance. Furthermore, the aqueous solutions of the sulfonates agreed exceedingly well with the Beer-Lambert Law, exhibiting, at the wavelength used, proportionality of absorbance to concentration.

The authors discovered that as the size of the para-alkyl group increases, the wavelength of maximum absorbance shifts. For example, p-toluenesulfonate absorbs at 220 mμ and 2-dodecylbenzene sulfonate absorbs at 225 mμ. Also, they state that it is imperative for the precision of experimental technique to clean all glassware and quartz cells with dihydrogen phosphate solution. This compensates for and removes any adsorbed sulfonates.

They describe a method for determination of alkylbenzene sulfonates which is much more simple and precise than quantitative analytic methods. However, this technique was carried out only on p-alkylbenzene sulfonates with the phenyl groups secondary on the carbon chain.

C. Solubility of Alkylbenzene Sulfonates

Shuck and Lingafelter (R-18) made a comparison of a polyalkylbenzene sulfonate to the colloidal electrolyte behavior of a n-alkylbenzene-p-sulfonate. This work was an attempt to describe the effect of decreased molecule size, without decreasing molecular weight, on micelle formation. They determined the solubility of Na tri-isopropylbenzene sulfonate in water over a temperature range of 10-49°C. The salt was found to act as a colloidal electrolyte.

Renich and Taft (R-16) investigated the solubility of p-toluene

sulfonate and found a strong temperature dependence over the range 0-15°C, which they attributed to probable hydrate formation. They found no evidence of micellular formation in the aqueous solutions.

The only two references that gave data on simultaneous solubility of an alkylbenzene sulfonate and an inorganic salt were Rhodes and Lewis, and Chang and Barduhn. Rhodes and Lewis (R-17) investigated the solubility of Na benzenesulfonate in water and in Sodium Sulfate solutions. They conducted the measurements over a temperature range of 0-105°C. The authors also worked on the dihydrate formation of NaBS at low temperatures.

Chang and Barduhn (R-15) investigated the solubility of sodium dodecylbenzene sulfonate in pure water over a temperature range of 0-25°C and solubilities of NaDBS in solutions containing varying amounts of NaCℓ at temperatures of 0° and 5°C. These data are shown in Figures 1 and 2, respectively.

The NaDBS used in the above study was obtained from K & K Laboratories and was believed to contain straight C_{12} chain. The crude NaDBS was made relatively free of inorganic salts, less than 0.05%, by extraction in a Soxhlet thimble with benzene as a solvent.

The concentrations of NaDBS in water and salt solutions were determined by using ultraviolet absorbance technique. The NaDBS exhibited a characteristic absorbance peak at 224 mμ, and a calibration curve for concentrations 0-50 mg/l was made at this wavelength. An absorbance curve for NaCℓ solutions was determined at 224 mμ and it was then observed that the absorbances of the organic and the inorganic in the NaDBS--NaCℓ--H_2O system were additive although the NaCℓ absorbance was negligible under

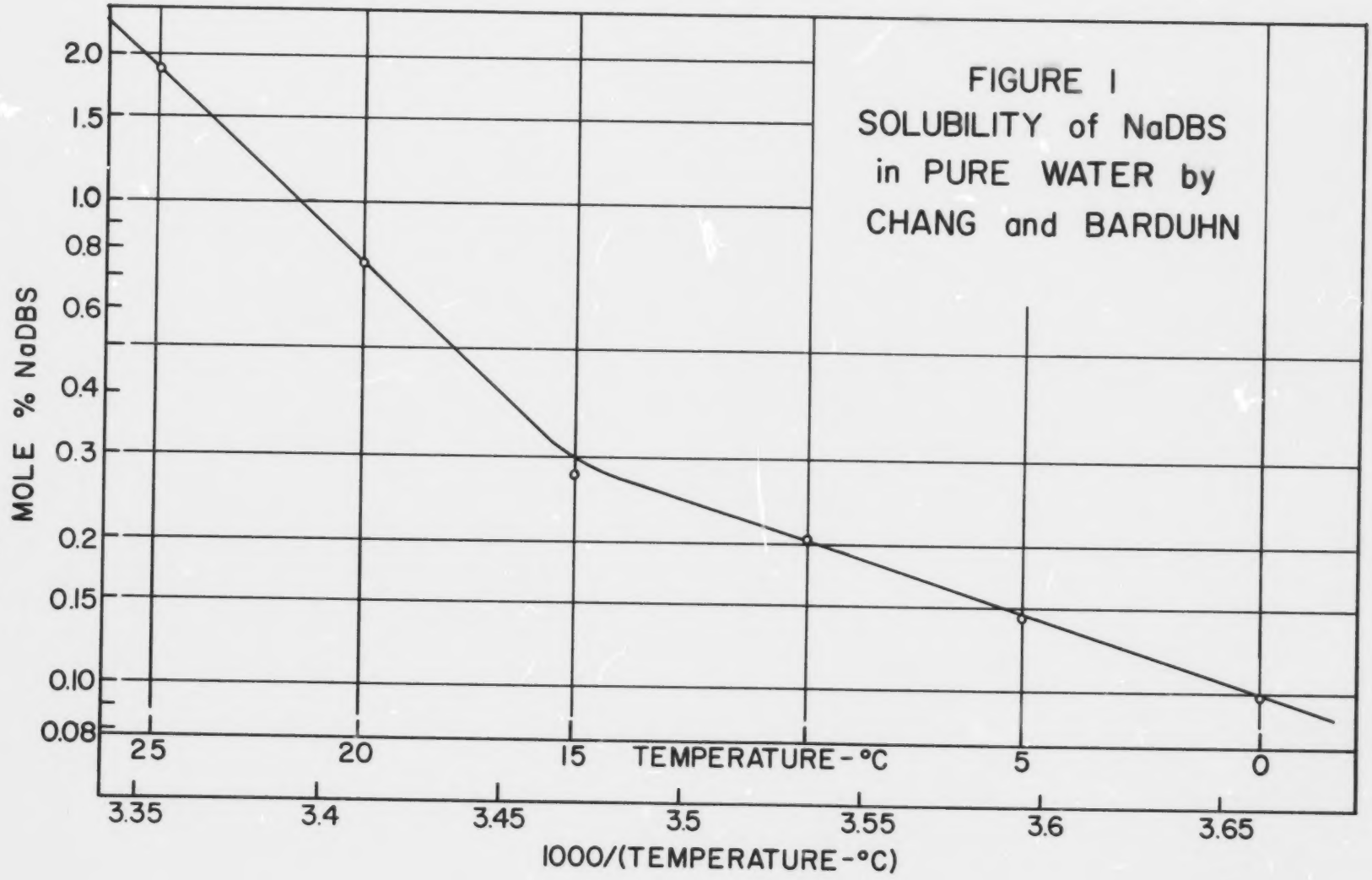


FIGURE 1
SOLUBILITY of NaDBS
in PURE WATER by
CHANG and BARDUHN
MOLE % NaDBS
2.0
1.5
1.0
0.8
0.6
0.4
0.3
0.2
0.15
0.10
0.08
25
20
15
TEMPERATURE - °C
5
0
3.35
3.4
3.45
3.5
3.55
3.6
3.65
1000/(TEMPERATURE - °C)

7-a

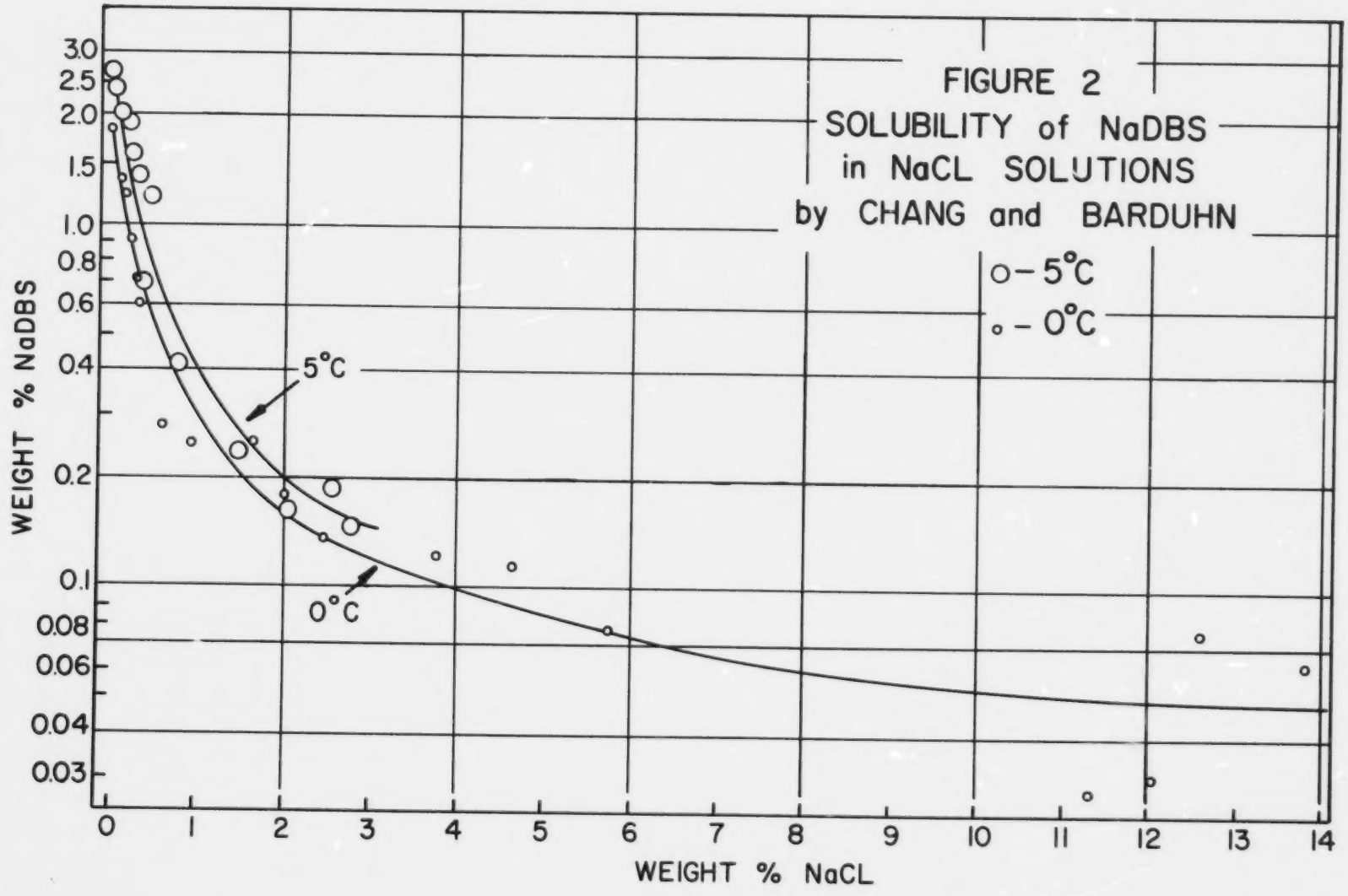


FIGURE 2
SOLUBILITY of NaDBS
in NaCL SOLUTIONS
by CHANG and BARDUHN
○ - 5°C
∘ - 0°C
5°C
0°C
WEIGHT % NaDBS
WEIGHT % NaCL
3.0
2.5
2.0
1.5
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.03
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14

most conditions. The absorbance of Na_2SO_4 at 224 mμ was found to be negligible under all conditions encountered.

The solution samples were prepared by placing an excess of NaDBS in a screw top test tube with a fixed amount of H_2O. At constant temperature the sample was shaken for 1 day and allowed to settle. A sample of the saturated solution was drawn off and analyzed. Varying amounts of NaCℓ may be added and the method repeated for simultaneous solubility determinations. When the concentration of NaCℓ was high, a correction for its absorbance was made where necessary.

They state that the consistency of the data for the NaDBS-H_2O system at low temperatures was poor and this was attributed to possible hydrate formation at these temperatures. However, the authors suggest the randomness may be caused by the presence of a water soluble impurity in the NaDBS. It was determined that extended shaking and settling time did not improve the random nature of the results.

The solubility of NaDBS in various NaCℓ solutions show poor consistency. They state only one determination was made at each salt concentration and suggest further work in the high salt concentrations is required to define the curves more accurately. An attempt was made to determine the composition of the solid phase NaDBS in the ternary system to check for the presence of a hydrate or double salt. The Schreinmaeker wet-residue was used but due to the flocculent nature of the solid phase it was impossible to get any reasonable results.

The problem of solubility of an alkylbenzene sulfonate being a function of the amount of excess solid phase present was not mentioned as

having been encountered by any of the workers discussed in this chapter. It appears that the investigators did not intentionally vary the amount of solids placed in excess but were more concerned with the extent of experimental and measurement errors.

D. Application of the Phase Rule to Ternary Systems

1. Variables of the System

When the organic-inorganic simultaneous solubilities are determined, there are three components, 2 salts and water, and the composition of every phase can be represented in terms of these components.

When a single solid co-exists with the saturated solution which consists of the three components, there exist 3 phases, vapor, an aqueous liquid solution and the solid. The Phase Rule states $F=C-P+2$, where

F = number of degrees

C = number of components

P = number of phases

Thus for the ternary system: F = 2. If the vapor phase were eliminated, F would be 3, but the effective number of degrees of freedom would still be 2 since pressure has little effect on the equilibrium among condensed phases. Hence by defining the concentration of one component in the solution and fixing the temperature, the system becomes invariant (F=0) and is completely defined.

If the system exists in a single aqueous phase plus vapor and the solution is unsaturated, the Phase Rule states

$$F=3-2+2=3$$

It is defined completely by fixing the temperature and the liquid composition with respect to both salts.

When the saturated solution is in equilibrium with two discreet solid phases, there co-exist four phases. Applying the Phase Rule

$$F=3-4+2$$
$$F=1$$

When the temperature is fixed, the system is invariant.

When conducting solubility studies on ternary systems which exhibit a single solid phase over a particular portion of the saturation curve, it is experimentally convenient to fix one salt concentration for a complete series of solubility determinations. For example, the concentration of NaCℓ in the aqueous solution for use in the NaDBS-NaCℓ-H_2O system is arbitrarily set (unsaturated). It has been found from the Phase Rule that the three component system while at constant temperature has zero degrees of freedom, and thus the solubility of NaDBS should be independent of the amount of the NaDBS in excess at equilibrium, since the extent of any phase is not a Phase Rule variable.

2. Geometric Representation of the System

The composition of a ternary mixture can be shown as a point in an equilateral triangle whose sides are 0-100% for each respective component. Other types of triangles have been utilized, such as right triangles, for representation of ternary systems. Provided

the apex represents a pure component, the side a binary and a point within the triangle a ternary system, all the methods of representation are identical whatever the shape of the triangle.

If neither the NaDBS nor the NaCℓ of the ternary system NaDBS--NaCℓ--H_2O forms a hydrate, the diagram on a right triangle illustrated in Figure 3A will represent the system. The apexes representing 100% NaCℓ or NaDBS need not appear and the origin shown represents 100% water.

3. System of Two Salts and Water

The kind of equilibrium for the ternary system of salts A+B and water W, that will be discussed in detail in this section, is the type with no chemical reaction or combination. Another classification, specifically one salt hydrate formation will be discussed briefly.

The solubility in the system of water and the two salts can be represented on an isothermal triangular diagram, Figure 3B. The apex points W,A and B denote pure components. Points a and b show the solubility for the binary systems A-H_2O and B-H_2O, respectively.

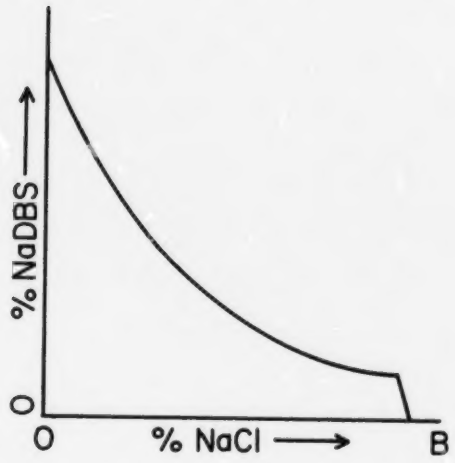
The isothermal saturation curve afb is obtained by starting with an unsaturated solution of one salt and adding the other salt until saturation is reached. For example, point d is obtained by starting with an unsaturated A salt solution and saturating it with salt B. At point f, the solution is saturated with respect to both salts, and there are two solid phases present. According to the Phase Rule, this point is invariant at constant temperature. The

system shown by point p and connected by tie line Ac, is composed of solid A in equilibrium with a saturated solution of composition c. By applying the inverse lever rule to the tie line Ac, the relative amounts of solid A (pc) and solution of composition c (Ap) are found. Also, point q is a system composed of saturated solution of composition d and of solid B. In the region of A+B+solution, point r consists of solid B, solid A and saturated solution of composition f. Using the inverse lever rule, the proportional amounts of solid B and solid A are found as Ag and Bg, respectively.

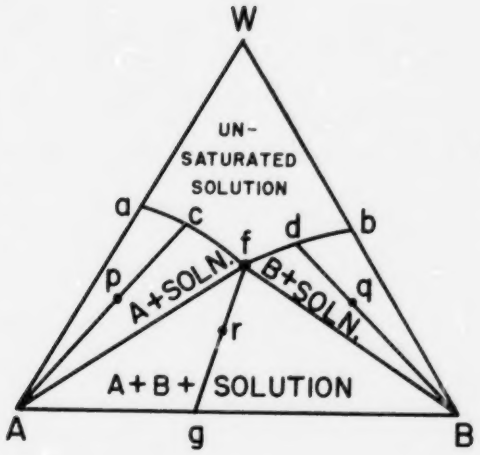
Removal of water at constant temperature from a ternary system is of primary importance to waste water purification processes. If one starts at k in the unsaturated solution region of Figure 3C and removes water at constant temperature (traversing along line Wo) no salt is precipitated until point ℓ is reached. When ℓ is reached A begins to precipitate and as more water is removed, the system arrives, for example, at m, where the system consists of solid A and saturated solution of m' connected by the tie line Am'. Upon further removal of water, point n is attained and B begins to precipitate. As more of the water is removed, A and B deposit simultaneously while the solution remains at composition f, and finally at o all the water has been withdrawn. Point f is termed a "drying up point". If one starts at p, similar behavior occurs along Ws. However, if one starts at x and traverses along Wy, no deposition occurs until point f is reached where A and B deposit simultaneously. Point y gives the final composition of the precipitated salts.

It may occur that A forms a hydrate H which is not affected by salt B, as illustrated by Figure 3D. The composition of the pure hydrate is denoted by H and its location depends on the amount of water of hydration. This diagram is similar to the one for the case of no chemical combination, in that line bf is the saturation curve for B and af is the saturation curve for H. The point f is invariant and in the region below this, the two solids H and B are present along with the saturated solution of concentration f. The region AHB is a completely solid mixture of A+H+B.

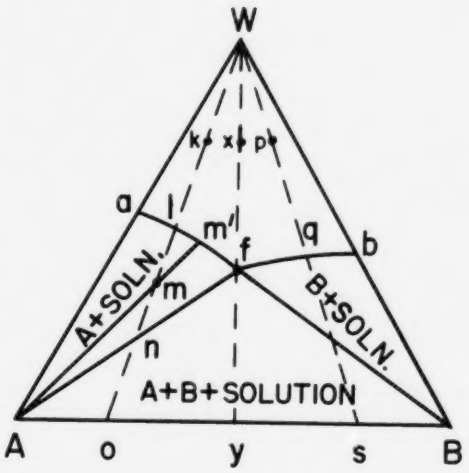
There are other general classifications where double salts are formed, the hydrates of double salts, etc.



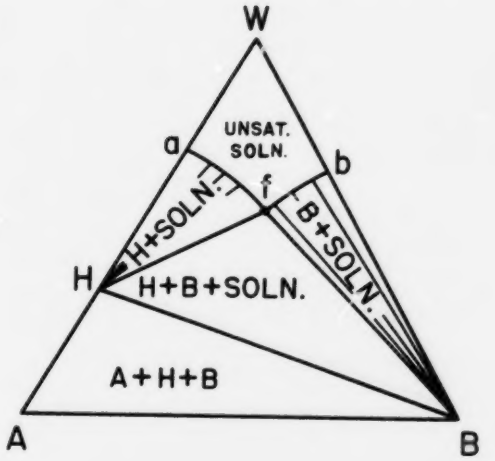
A - TRIANGULAR DIAGRAM



B - TWO SALTS and WATER



C - REMOVAL of WATER at CONSTANT TEMPERATURE



D - HYDRATE(H) not DEHYDRATED by SALT B

FIGURE 3
TERNARY SYSTEM DIAGRAMS

III. EXPERIMENTAL WORK

Commercially prepared NaDBS is a mixture containing ortho and para sulfonate isomers, several homologs, and isomers differing in side chain structure. These homologs consist of alkyl groups varying from ten to fifteen carbon atoms. There is no simple method for successfully resolving such a mixture into its pure components. This commercial ABS would not serve as a good starting material for solubility studies.

Chang used a purified form of crude NaDBS containing 5% inorganic salts and 30% water. It was believed to contain only the straight chain 1-dodecyl alkyl group. This product was purified, after the water was evaporated, by extracting the NaDBS in a Soxhlet thimble. The solvent, benzene, dissolves the organic and leaves the inorganics behind. Since the solubility results obtained with this purified NaDBS were non-reproducible in pure water and salt solutions, it was presumed that the inconsistency was due to soluble impurities or to both ortho and para isomers being present.

At the beginning of this work, efforts were made to improve the purification procedures of Chang. The material used in this portion of the study was from the same batch of NaDBS prepared by K & K Laboratories. Petroleum ether was used as a de-oiling agent prior to soxhlet extraction. The technique was further altered by switching the extraction solvent from benzene to anhydrous ethyl alcohol and then to anhydrous diethyl ether. Also, a convenient check on the sample purity was utilized in the preparation procedure for solution samples. True solubility of a pure compound should be independent of the amount of excess solid phase present. For

example, the solubility of two systems, with identical components, one with an excess of 10 gms and the other with a 100 gm excess, should be the same. It was found that the solubility of the NaDBS would increase with a corresponding larger excess solid phase present at equilibrium. This behavior in pure water was found to occur with the NaDBS purified, not only according to Chang's procedure but persisted even after the more elaborate purification methods were applied.

It was felt that perhaps it was a kinetic effect and that more shaking time and large excesses of solids would result in an asymptotic maximum solubility. Samples were prepared with large excesses where solid-liquid separation was possible only through extensive centrifuging. However, no maximum was obtained, the solubility continued to change with increasing excess solid phase.

It was then concluded that the starting material was not a single pure compound but was a mixture of two or more compounds, one of which was extremely soluble. This could account for the large excess necessary to achieve equilibrium with respect to both compounds. Therefore, because of the requirement to have the organic component a single compound it was necessary to synthesize a pure isomer of NaDBS in the laboratory. In so doing, it was hoped that the problem posed by the anomalies would be solved and consistent and reliable data could be obtained.

The preparation of the isomeric sulfonates of 1-phenyldodecane, to be used in the solubility studies, was adapted from the synthesis described by Gray, Gerecht and Krems (R-5).

The 1-phenyldodecane used in this work was purchased from

Distillation Products, Inc. They prepared this compound by a Friedel-Crafts reaction between benzene and lauric acid, followed by a Wolff-Kishner reduction of the laurophenone. The gas chromatographic analysis of their product shows 2.5% impurities or 97.5% pure 1-phenyldodecane (R-7).

The infrared spectrum of 1-phenyldodecane, shown in Figure 4, displays characteristic absorbances at 13.45, 13.85 and 14.36μ. This is identical to the standard spectrum published by the American Petroleum Institute (R-1). It can be shown that the spectrum of a 1-phenylalkane differs in the 13-15μ region from those phenylalkanes in which the phenyl group is attached to a carbon possessing two alkyl groups. However, differentiation of these phenylalkanes, in which the phenyl is attached to a carbon connecting two alkyl groups is rather tedious. The spectrum of the 1-phenyldodecane was determined on a 521 Perkin Elmer Infrared Spectrophotometer using a NaCℓ cell.

A. Preparation of NaDBS

1. Sulfonate Synthesis and Extraction Procedures

In the sulfonation apparatus, Figure 5, 100 gms of 1-phenyldodecane were placed. At an initial temperature of 15°C, 101 gms of 20% oleum were added gradually to the hydrocarbon by means of a dropping funnel. During the acid addition, approximately 20 minutes, the temperature of the mixture was not allowed to rise above 30°C. After the addition, the temperature was raised to 50°C and held there for 2 hours. Also at this time the funnel was replaced by a condenser.

The sulfonic acid mixture was neutralized with aqueous NaOH

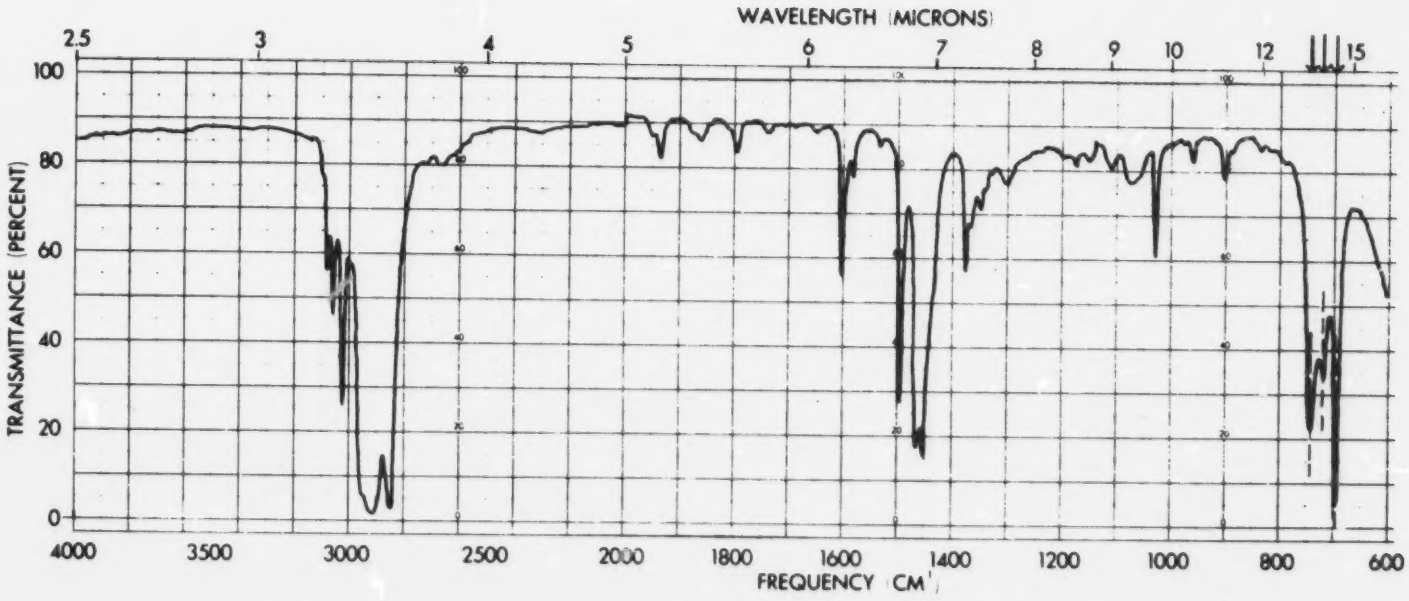
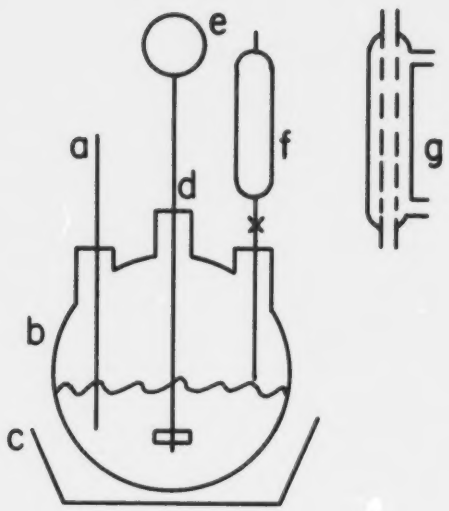


FIGURE 4:
INFRARED SPECTRUM
of 1-PHENYLDODECANE



a- Thermometer
b- 1000 ml, 3-Neck Flask
c- Temperature Bath
d- Stirrer, Ground Glass Joint
e- Motor
f- Dropping Funnel
g- Condenser, Replaces Funnel After Addition of Acid

FIGURE 5

SULFONATION APPARATUS

16-b

(10 wt.%) to a pH of 7. Care was taken not to overheat the mixture during the salting process. To serve as a safety precaution and to alleviate the possibility of isomerization both caused by high temperatures, the neutralization flask was placed in an ice bath. The para isomer precipitates and was separated from the mother liquor by vacuum filtration on a Buchner funnel. The mother liquor, containing the ortho isomer, was dried in an oven at 90°C. The residue was placed in a Soxhlet Extraction apparatus and extracted with anhydrous ethyl ether. The ether dissolves the ortho isomer and leaves the Na_2SO_4 and the residual para behind. Also, the previously separated para was extracted with ether to remove any ortho isomer brought down during precipitation.

The ether soluble portion was dried in a hood and the residue was extracted with ether a second time in the Soxhlet thimble. Again the ether soluble portion was dried. This was contacted with ether a third time. This ether effluent was contacted 4 times with double distilled water in a separatory funnel. The o-NaDBS was in the aqueous layer and ether layer contains oils, sulfones, etc. This aqueous portion was dried and finally dissolved in anhydrous ethyl alcohol. The alcohol solution was filtered leaving behind any inorganic salts as residue. This alcohol soluble portion was dried, giving pure o-NaDBS for solubility studies. A total of 500 gms of 1-phenyldodecane were sulfonated, and the isolated products of the reaction were 90 gms (13%) of o-NaDBS and 540 gms (78%) of p-NaDBS.

The para isomer can be purified by recrystallization from hot

water. The extraction procedures discussed are the best available at the present time. There was no method found which enables one to determine a small amount of an inorganic sulfate in the presence of a large amount of an organic sulfonate.

2. Identification of o-NaDBS

The para isomer was found to be a white crystalline powder which is insoluble in most organic solvents and water. This primary para isomer exhibits a characteristic absorption doublet at 11.90μ and 12.28μ (R-5). The ortho isomer, a sticky, hygroscopic, yellow compound, was identified by its infrared spectrum shown in Figure 6. This isomer exhibits its characteristic peak at 13.36μ, and no peak formation at the characteristic para wavelengths was observed in the ortho samples. This spectrum agrees very well with that of Gray, Gerecht and Krems (R-5). The infrared spectrum was obtained on a 521 Perkin Elmer IR machine using a film sample technique on a KBr disc.

For comparison, the NaDBS product used by Chang was analyzed to investigate the presence of the para isomer. A portion of NaDBS produced by K & K Laboratories was dissolved in alcohol. The same film sample technique on KBr discs was used. The spectrum, shown in Figure 7, displays a para band at 12μ along with the primary ortho band at 13.36μ. The spectrum agrees quite favorably with the qualitative classification of surfactants by infrared spectra shown in Table I (R-2).

The single para absorption peak at 12μ may be due to a number

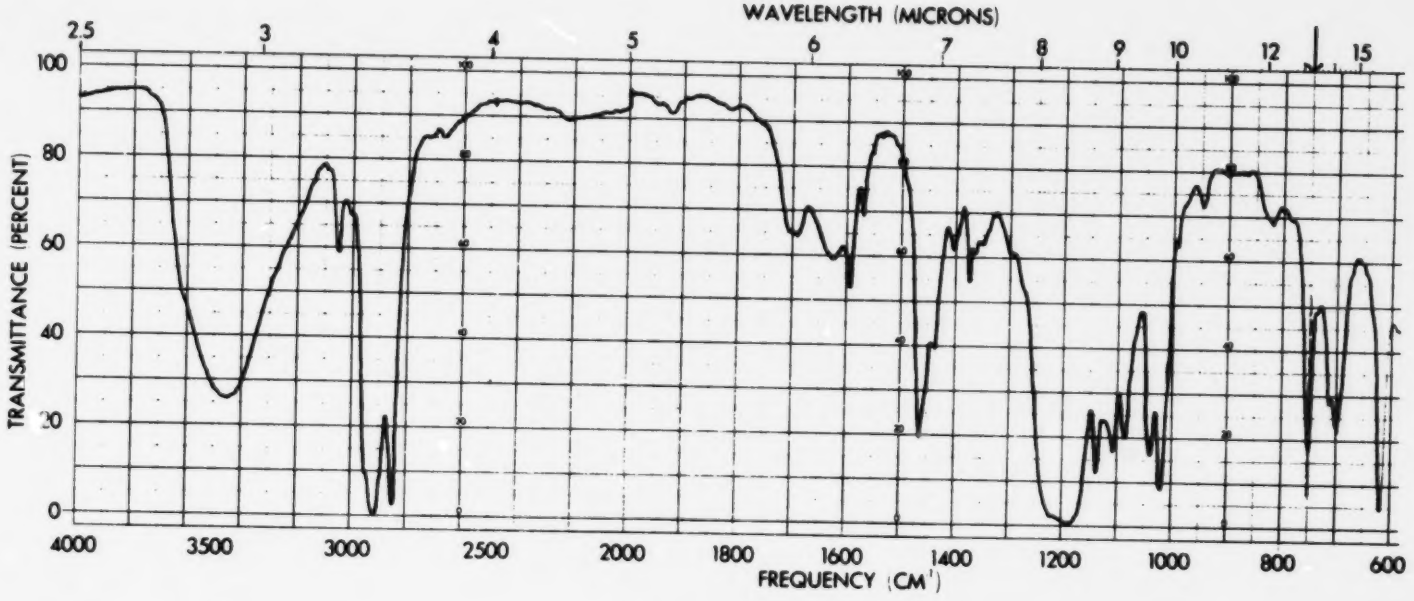


FIGURE 6:
INFRARED SPECTRUM
of SODIUM o-DODECYL BENZENE
SULFONATE

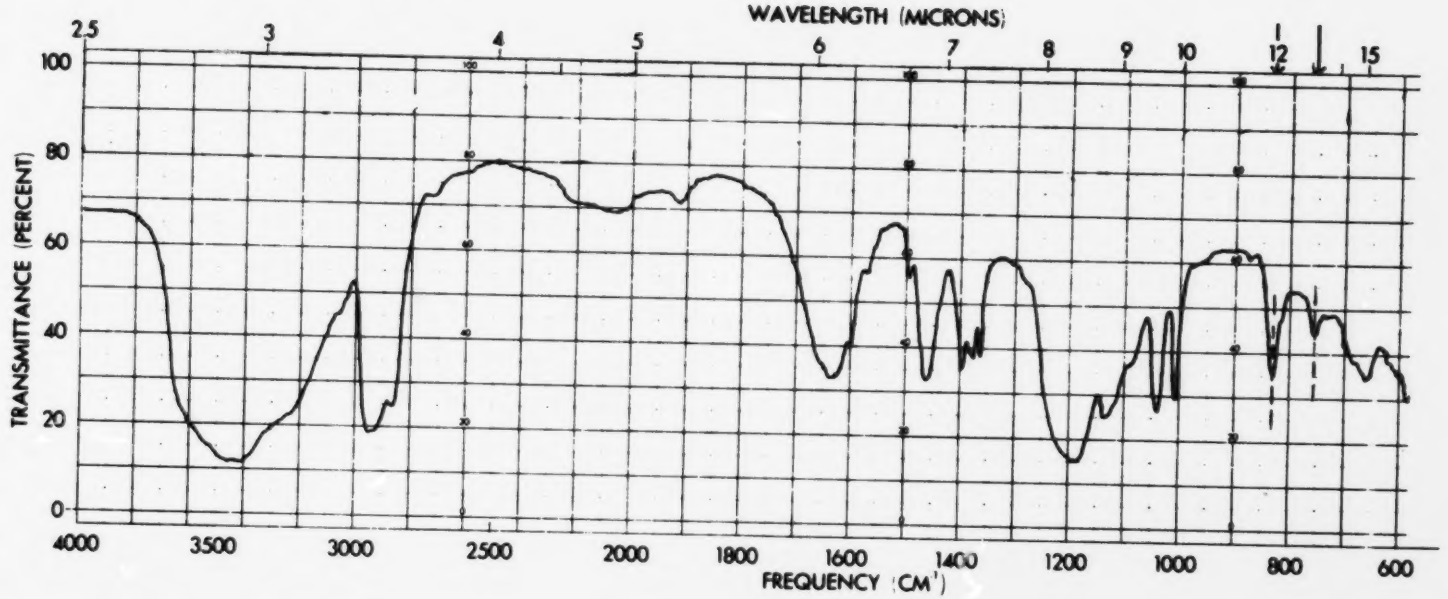


FIGURE 7:
INFRARED SPECTRUM
of NaDBS PRODUCT
FROM K&K LABORATORIES

TABLE I

INFRARED ABSORPTION BANDS OF TYPICAL COMMERCIAL DETERGENTS

Detergent	Wave Length μ	Frequency cm^{-1}	Band Shape	Band Intensity	Identity
Alkylbenzene Sulfonate	6.7	1493	shoulder	weak	aromatic bands
	8.1 to 8.5	1235-1176	broad	strong	sulfonate group
	8.8	1136	sharp	moderate	sulfonate group
	9.6	1042	sharp	strong	ABS bands
	9.9	1010	sharp	strong	ABS bands
	12.0	833	broad	moderate	para substitution

of isomers, excluding those alkylbenzene sulfonates with primary phenyl group position, of para orientation which are soluble in alcohol. The compound, for example, Na-p-(1-methyldodecyl) benzene sulfonate, which is more soluble than p-NaDBS, will exhibit such a peak. A mixture containing these isomers and homologs would cause the solubility data to be highly lacking in reproducibility.

To insure validity of the o-NaDBS spectrum and to secure a measure of the purity of the ortho salt, ether and alcohol solutions of o-NaDBS with 2 and 10% p-NaDBS by weight, were investigated. However, the para isomer did not dissolve in the solvents which made its detection impossible. This does point out that the para isomer should have been successfully removed from the ortho salt by the extraction techniques.

B. Analysis of NaDBS Solutions

A portion of the experimental work of this study is concerned with the determination of the NaDBS concentrations in pure water and in aqueous NaCℓ solutions. Previous UV work showed a maximum for commercial ABS and the purified NaDBS from K & K Laboratories, at 224 mμ. Accordingly, the absorbance of an aqueous o-NaDBS solution (50 mg/l) was measured at many points over the 210-290 mμ range. It was found that no maximum absorbance was exhibited at 224 mμ but a plateau was observed in the 214-216 mμ range. The lowest possible wavelength with the machine used was 214 mμ. This, of course, caused some speculation as to the applicability of the UV method. However, upon careful scrutiny, it was found that Weber and co-workers investigated only p-alkyl oriented groups. Upon investigation of p-NaDBS in

the UV range it was found that maximum absorbance occurred at 223 mμ. Also, the K & K Laboratories NaDBS and DS-10 by Alcolac Corp., NaDBS products known to contain para isomers, exhibited maximum absorbance at 224 mμ as expected. The absorbance spectra of o-NaDBS and p-NaDBS are shown in Figures 8 and 9 (also see Appendix A).

Therefore, a calibration curve of o-NaDBS absorbance at 216 mμ for known concentrations (0-50 mg/l) was made. A second sample was made up and the calibration repeated; the reproducibility of the data was well within the limits of experimental error.

The absorption of the Na_2SO_4 in the UV range of 215-290 mμ was studied and found to be negligible at the concentrations and experimental conditions expected. Then the absorbance of NaCℓ solutions was measured at 216 mμ and it was found that its absorbance can be ignored for most conditions expected. However, when dealing with concentrated NaCℓ solutions in the range 14-25 wt.%, corrections are required for the absorption by the NaCℓ in the diluted samples. The absorbance of NaCℓ-NaDBS solutions was assumed to be additive at 216 mμ because of the additive property found at 224 mμ (R-15). Absorbance data (calibration curves) for o-NaDBS and NaCℓ are listed in Tables II, III and shown in Figures 10 and 11, respectively. The transmittance data for Na_2SO_4 are listed in Table IV.

The UV absorbance work was done on a Beckman DU Quartz Spectrophotometer. Double distilled water was the standard (100% Transmittance).

When working with saturated liquid solutions of the presumably pure o-NaDBS in water, the liquid phase sample is taken, weighed accurately and

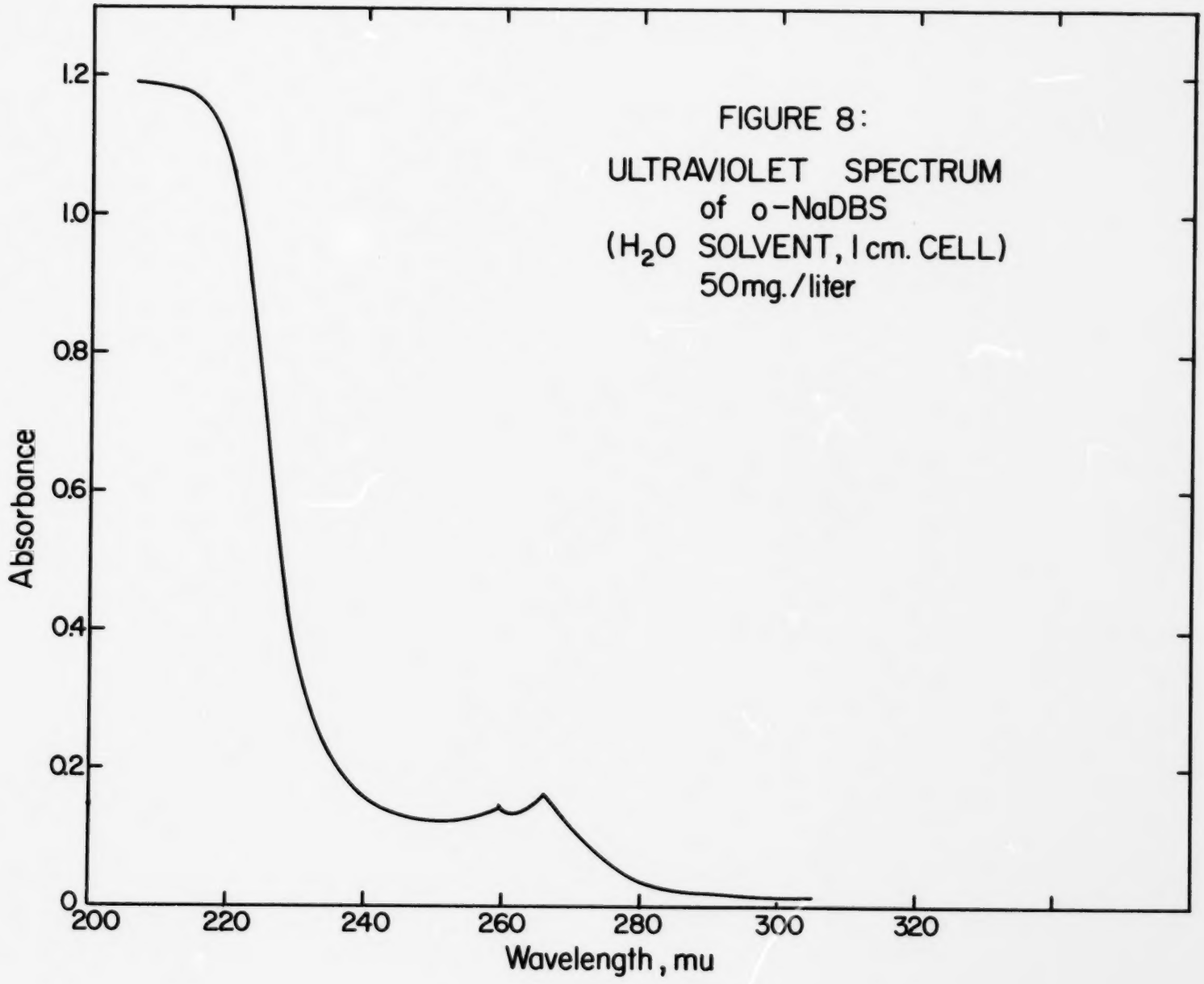


FIGURE 8:

ULTRAVIOLET SPECTRUM
of o-NaDBS
(H_2O SOLVENT, 1 cm. CELL)
50 mg./liter

21-a

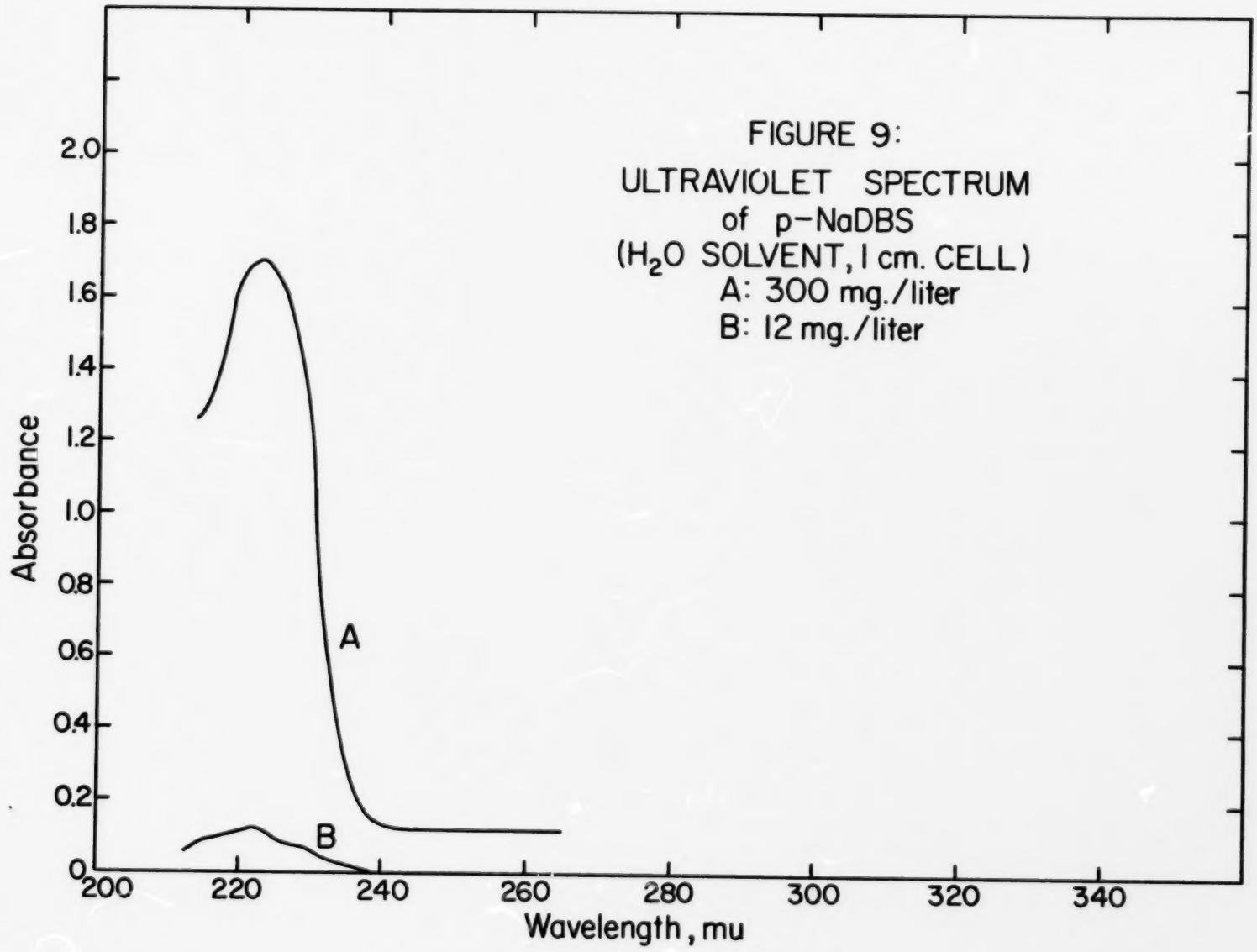


FIGURE 9:
ULTRAVIOLET SPECTRUM
of p-NaDBS
(H_2O SOLVENT, 1 cm. CELL)
A: 300 mg./liter
B: 12 mg./liter

21-2

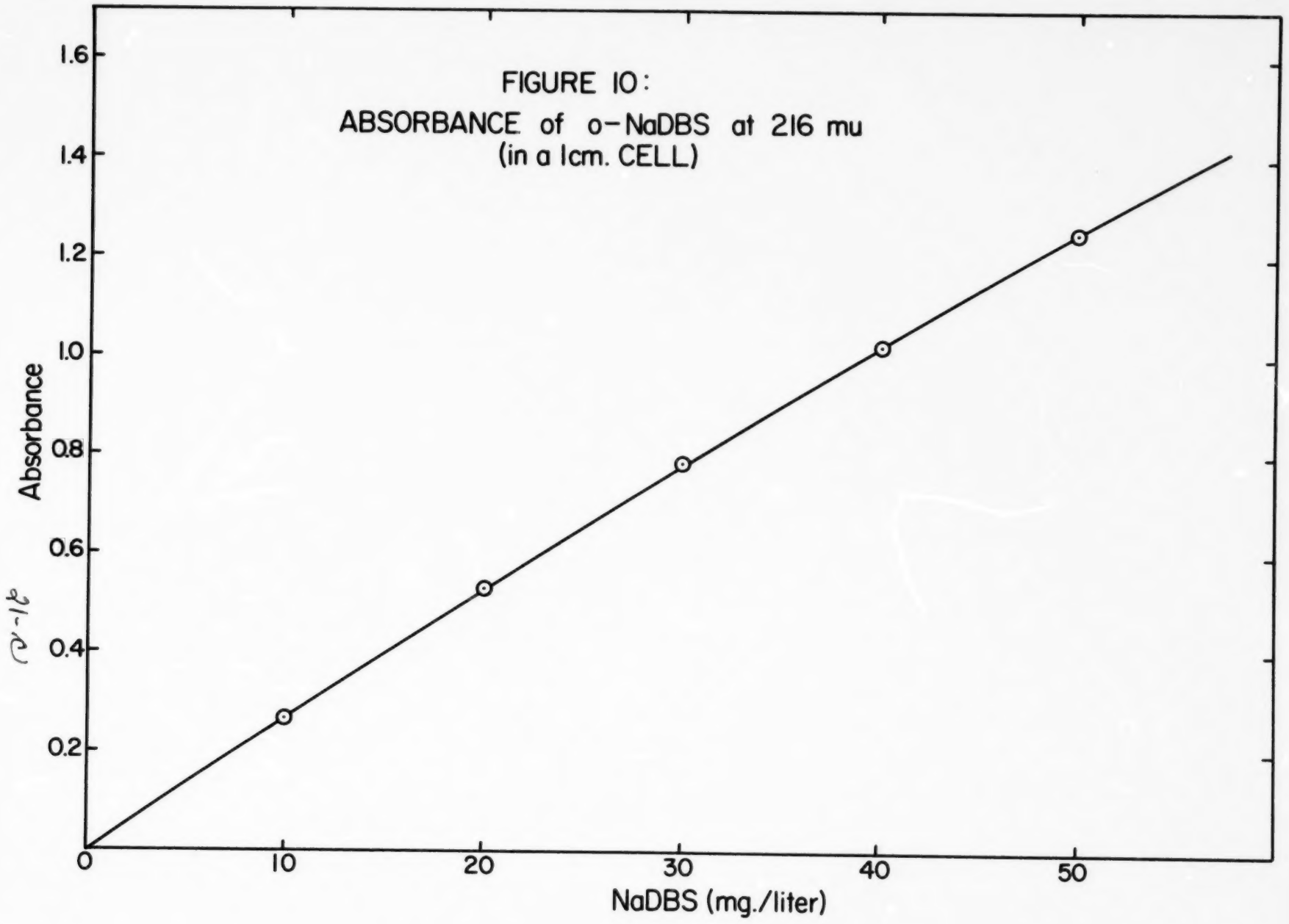


FIGURE 10:
ABSORBANCE of o-NaDBS at 216 mu
(in a 1cm. CELL)
Absorbance
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
10
20
30
40
50
NaDBS (mg./liter)

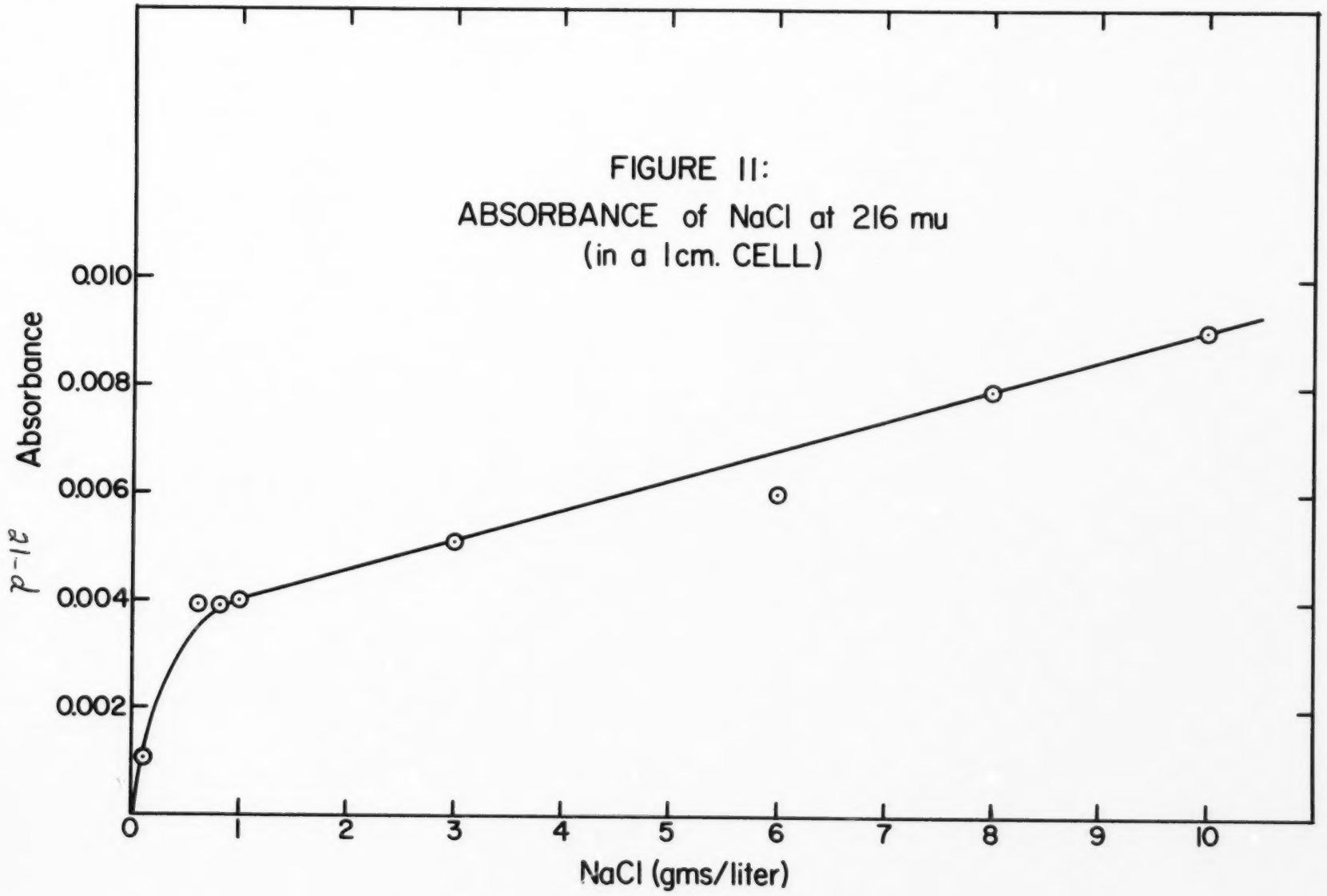


FIGURE 11:
ABSORBANCE of NaCl at 216 mu
(in a 1cm. CELL)
Absorbance
0.010
0.008
0.006
0.004
0.002
0
1
2
3
4
5
6
7
8
9
10
NaCl (gms/liter)

P-12

TABLE II

ABSORBANCE OF PURE o-NaDBS SOLUTIONS

C = conc.NaDBS (mg/ℓ)	A = Absorbance at 216 mμ in 1 cm cell	C = conc.NaDBS (mg/ℓ)	A = Absorbance at 216 mμ in 1 cm cell
0	0.0	40	1.02
10	0.267	50	1.25
20	0.531	100	1.91
30	0.790		

The following equation fits the above data with a maximum error of 1.4%.

$$A = 0.0277C - 5.47 \times 10^{-5}C^2$$

TABLE III

ABSORBANCE OF NaCℓ SOLUTIONS AT 216 mμ(1 cm cell)

NaCℓ conc.(gm/ℓ)	Absorbance	NaCℓ conc.(gm/ℓ)	Absorbance
0.00	0.00	1.0	0.004
0.1	0.001	3.0	0.005
0.3	0.0025	6.0	0.006
0.6	0.0039	8.0	0.008
0.8	0.0039	10.0	0.009

TABLE IV

ULTRAVIOLET ABSORBANCE OF Na_2SO_4(1.01 gm/100 cc H_2O ; 1 cm cell)

mμ	T%	Absorbance	mμ	T%	Absorbance
215	97.5	0.01	230	98.9	0.005
218	97.6	0.01	240	99.1	0.004
220	98.2	0.007	250	99.3	0.003
222	98.5	0.006	260	99.5	0.002
224	98.8	0.005	270	99.7	0.001
226	98.8	0.005			

diluted. This dilution is extended to a concentration of o-NaDBS that could be analyzed within the sensitivity limits (10-50 mg/l) of the spectrophotometer. Also for the NaDBS--NaCℓ--H_2O system, the liquid phase sample is taken, accurately weighed and diluted, usually to 100 cc. This dilution brings the o-NaDBS concentration, for 1 gm samples within the 10-50 mg/l range. The NaCℓ concentration is determined by titration with a standard $AgNO_3$ solution. After the NaDBS absorbance is obtained and an absorbance correction due to the NaCℓ is made, where necessary, the o-NaDBS concentration is determined by reference to the calibration curve. The solubility of the organic in the saturated solution is then readily calculated. Appendix B shows a typical set of data taken when a run is performed and the calculations that are made with them.

Care must be taken to obtain a sample of the saturated solution that is free of o-NaDBS particles. Inclusion of these particles in the sample will yield a higher NaDBS concentration and lower NaCℓ content than is actually present at equilibrium. Also, all glassware and quartz cells should be cleaned with a chromic acid solution to remove soap films and other contaminants which tend to decrease the precision and accuracy of analytic technique.

C. Experimental Procedure for Solubility Measurements

1. o-NaDBS--H_2O

The method used for determining the solubilities is to place an excess of NaDBS with a fixed amount of water in a 50 cc screw top test tube. In the preparation of a set of solution samples (4 or 5 tubes), the quantity of o-NaDBS placed in each tube is varied such

that the solid phase present at equilibrium ranges from a trace to a large amount. This graduated excess solids scheme serves as a purity check on the NaDBS starting material because the solubility of a pure compound should be independent of the amount of it in excess at equilibrium. The sample tubes are made water-tight and then placed on a rocker submerged in the constant temperature bath and shaken usually for 24 hours. Extended periods of shaking on the order of 5 days, showed no significant changes in solubility. This rocker is a plastic plate pivoted at the center and attached to a crank which is driven by a 15 r.p.m. motor. The motion of the plate is a "see-saw" type of oscillation.

The samples were removed from the rocker and allowed to settle at the same constant temperature in a submerged test tube rack. At high temperatures, such as 15°C, the settling was slow and time consuming due mainly to the high viscosity of the solution. The samples required from 4 to 6 weeks to settle before a clear supernatant solution was obtained. After sufficient separation, a sample of the saturated solution was drawn off and analyzed.

Temperature variation of the temperature bath is not greater than 0.02°C. The temperature bath, Model No. 2073B, was purchased from the Forma Scientific Company. A 1/3 H.P. agitator was added in order to supplement the circulation of bath medium. The bath medium was ethylene glycol-water solution.

2. o-NaDBS--NaCℓ--H_2O System

The preparation procedure for these samples is much the same as

that used for o-NaDBS--H_2O system samples. An excess of the solid o-NaDBS is added to a 20 cc volume of a specific NaCℓ solution. Usually for a particular group of samples at fixed NaCℓ concentration, the amount of o-NaDBS added per tube ranges from 0.5 to 10 wt.% of the total mixture placed in the respective tube. Agitation is for 48 hours. The settling time for these samples, due to the low solubility of the organic in saline solutions, is relatively short and on the order of 1-3 days.

When conducting studies on the three component system at NaCℓ concentrations of 4.5% and above, it was observed that the solid o-NaDBS particles would often float on the surface of the saturated solution. This made it difficult to remove a sample of clear solution but inspection of the solution sample to be analyzed plus repeated sample measurement provided a reasonable check.

IV. PRESENTATION AND DISCUSSION OF RESULTS

A. Solubility of o-NaDBS

1. In Pure Water

The solubility of o-NaDBS in pure water at 0°C is listed in Table V. The results are random but it is evident from the data that the solubility of the ortho salt becomes larger with increasing amounts of solid phase. Nevertheless, these results do show that the o-NaDBS is much more soluble than the compound investigated by Chang. The solubility of o-NaDBS is greater by a factor of about 8-1/2 times the value reported for the NaDBS produced by K & K Laboratories and purified with benzene.

TABLE V

SOLUBILITY OF o-NaDBS IN PURE WATER AT 0°C

Sample No.	gms o-NaDBS per 20 cc H_2O	wt.% o-NaDBS in mixture	Sol.of o-NaDBS, wt.%
1	3.74	15.7	14.1
2	5.32	21.0	15.3

Chang reported 1.86 wt.% NaDBS product (K & K Laboratories)at 0°C

It is apparent from the results that the solubility of o-NaDBS increases with larger excesses of solid phase present. However, such anomalies in solubility behavior are not alien to the experimental solubility results obtained with NaDBS. For the first year on this project, the author has experienced the same qualitative behavior with the NaDBS product of K & K Laboratories which was purified according to the procedures outlined in Chapter III.

Chang and Barduhn had difficulty in obtaining consistent solubility results at low temperatures in both pure water and NaCℓ solutions. By design, the amount of NaDBS placed in the test tube with a fixed quantity of water was a relatively constant value. The inconsistencies in both systems prompted a re-examination of the procedures and purity of the NaDBS product, and eventually led to the anomalies in solubility observed by the author.

In the present study with the highly soluble ortho salt, the solutions were found to be viscous and settling times were on the order of 4-6 weeks. Further work with the organic component in pure water thus would be slow and the main goal was to observe the effect on inorganic salts on NaDBS solubility. It was thus decided to work immediately with the ternary system since the solubilities and viscosities would be much lower and data could be taken at a much faster rate.

2. In NaCℓ Solutions

The solubility of o-NaDBS in salt solutions of fixed concentration was measured at 0°, -10° and -20°C. It should be noted that the changing solubility of the ortho salt with increasing solid phase present continues to prevail, as it did in the pure water system. However, the results do show the effect of NaCℓ on the o-NaDBS solubility. The NaCℓ salts out the soluble organic markedly. At 0°C, 4.5% NaCℓ reduces the solubility of the NaDBS by a factor of 28 for the 10 wt.% total NaDBS in mixture sample, and for 14% NaCℓ the solubility is reduced by a factor of 98 for the sample with 8% total

NaDBS in mixture.

These results as they stand are not directly useful, since the excess solid phase affects the results. One method of putting the data onto a common basis is to plot solubility versus excess solid and extrapolate to 0% excess. This is best done by plotting log % solubility versus wt.% excess solid phase o-NaDBS (based on the total weight of mixture). Then the curves are drawn and extrapolated to 0% excess solids present. Figures 12, 13 and 14 show the extrapolations of the curves at fixed salt concentrations for 0°, -10°, and -20°C. The extrapolated points, termed 0% excess, and the solubility of o-NaDBS in NaCℓ solutions are given in Table VI.

The % excess o-NaDBS abscissa points were calculated assuming the weight of the specific salt solution added was a constant, for example, 20 cc of 14% NaCℓ (ρ = 1.1) weighed 22 gms, and then a material balance to obtain the amount of NaDBS in solution was made. It is hoped that these points with 0% excess solids, lower in magnitude than the points on the curve, may be useful in design calculations for the freezing process. Presumably they represent the conditions for the initial precipitation of o-NaDBS as water is removed from a solution.

The solubility of o-NaDBS (0% excess solid phase) is lower than the % NaDBS at corresponding salt solution concentrations reported by Chang. It should be noted that his samples did possess solid phase excesses. The solubility of o-NaDBS (0% excess solids) in salt solutions is given by Figure 15.

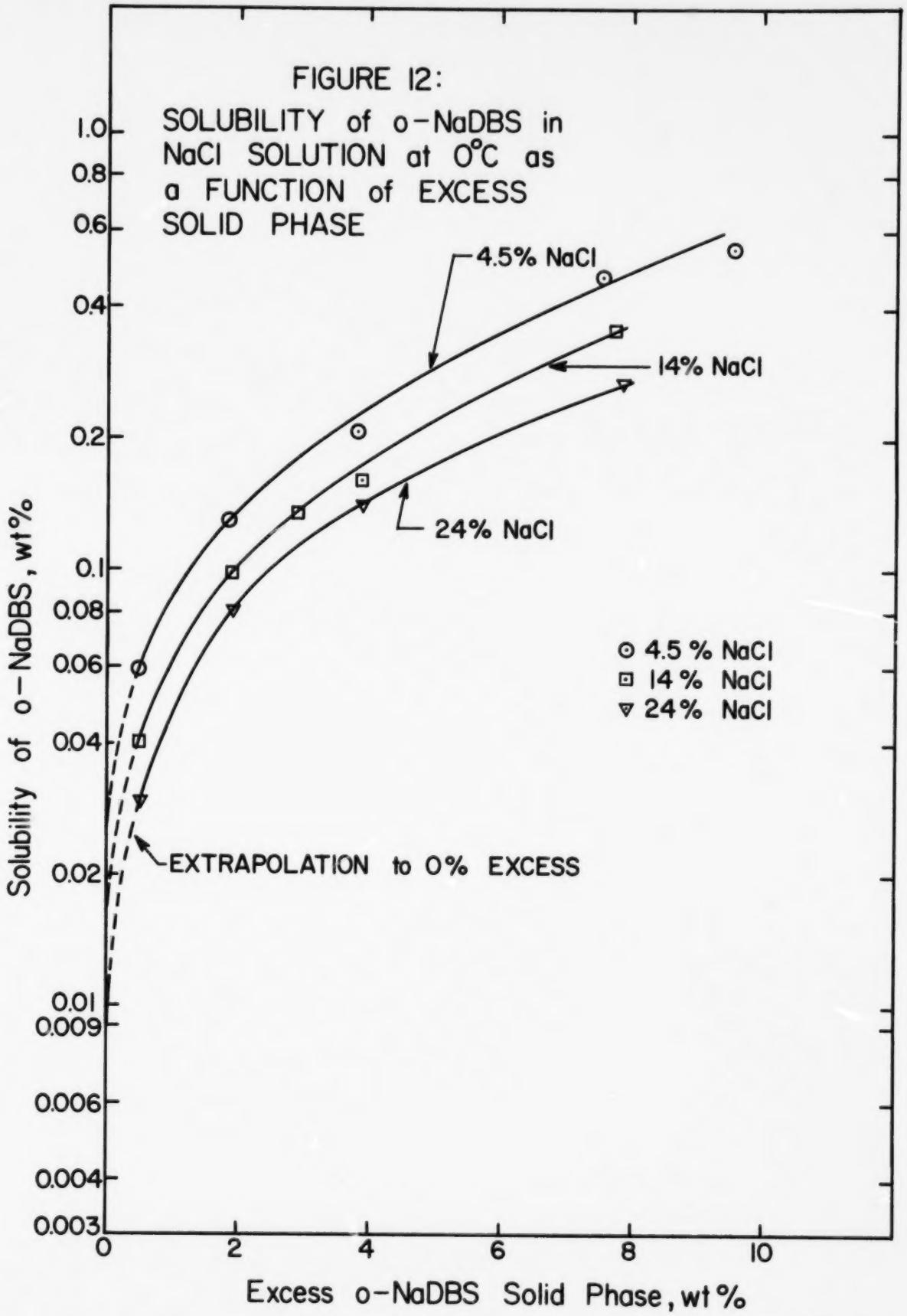
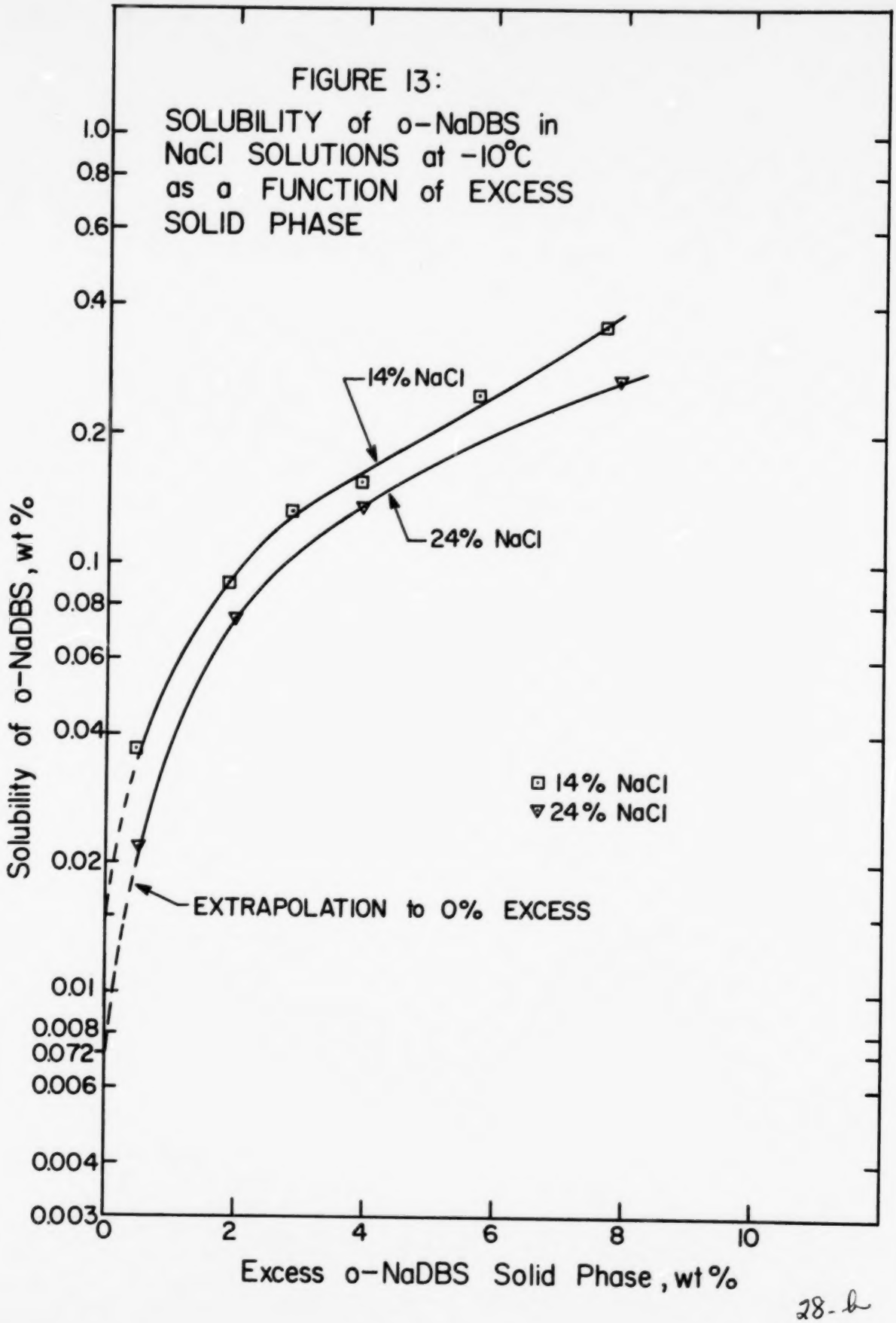


FIGURE 12:
SOLUBILITY of o-NaDBS in NaCl SOLUTION at 0°C as a FUNCTION of EXCESS SOLID PHASE
4.5% NaCl
14% NaCl
24% NaCl
⊙ 4.5 % NaCl
⊡ 14 % NaCl
▽ 24% NaCl
EXTRAPOLATION to 0% EXCESS
Solubility of o-NaDBS, wt%
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.009
0.006
0.004
0.003
0
2
4
6
8
10
Excess o-NaDBS Solid Phase, wt %

28-a

FIGURE 13:

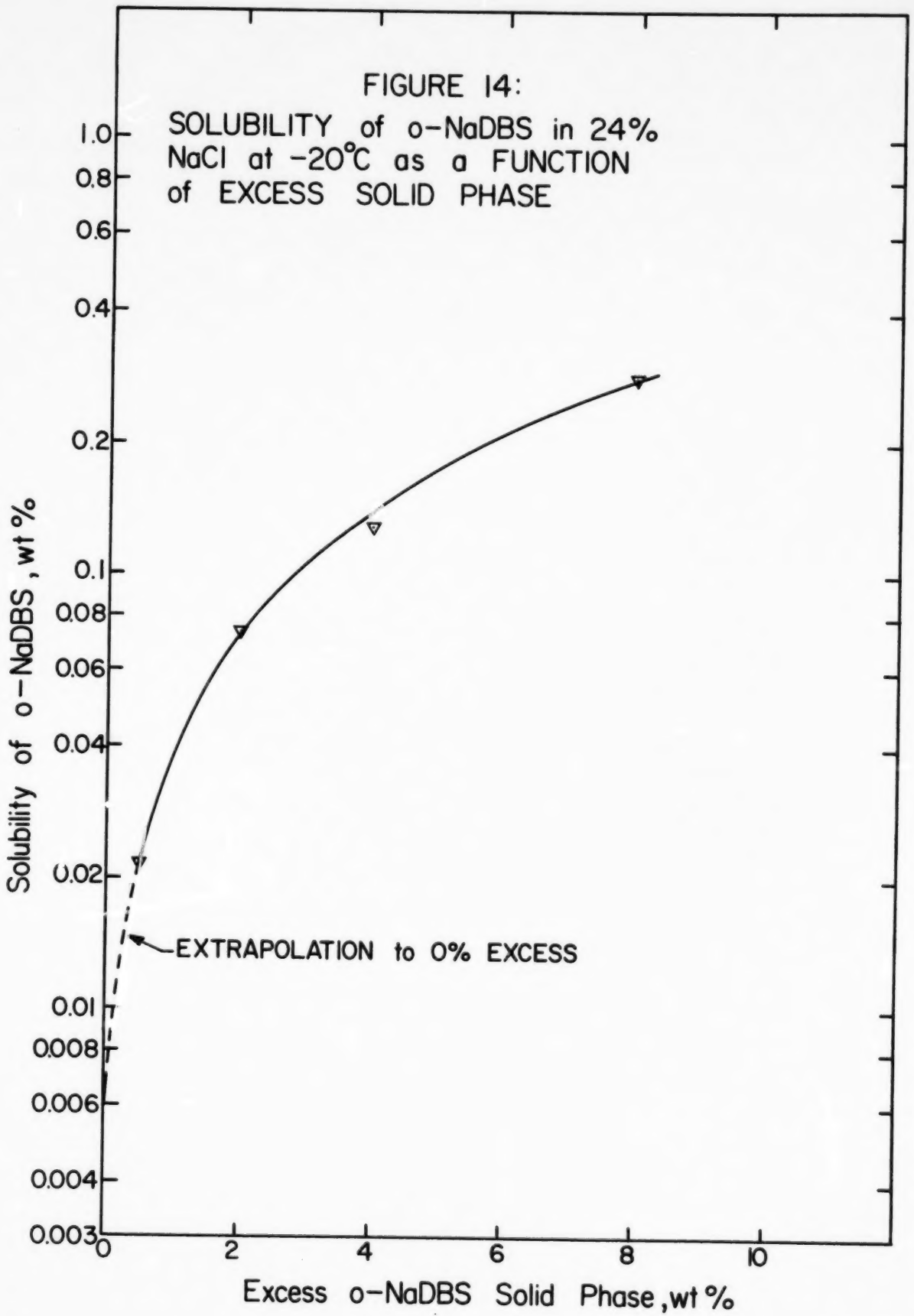
SOLUBILITY of o-NaDBS in NaCl SOLUTIONS at -10°C as a FUNCTION of EXCESS SOLID PHASE



28-b

FIGURE 14:

SOLUBILITY of o-NaDBS in 24% NaCl at -20°C as a FUNCTION of EXCESS SOLID PHASE



28-C

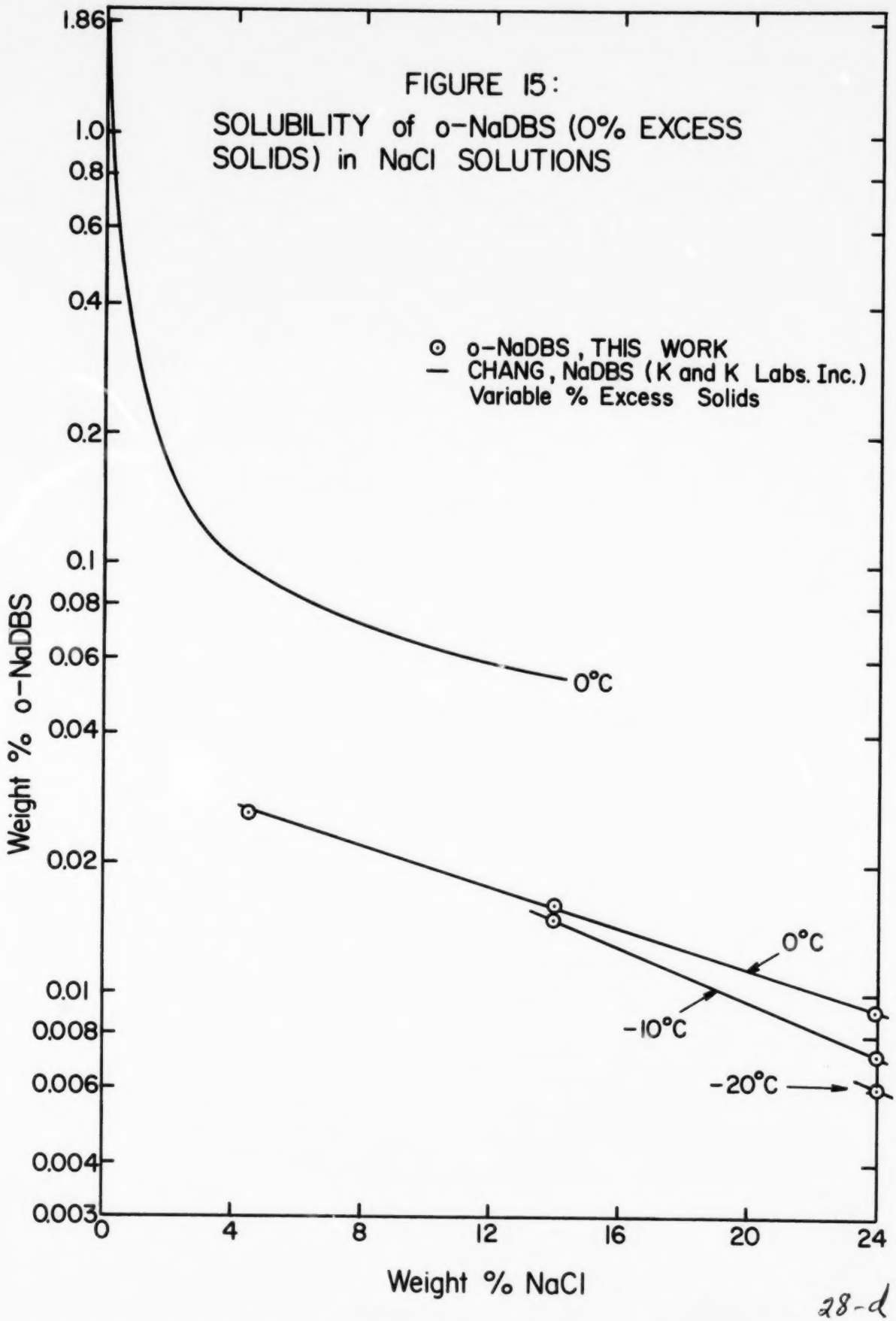


FIGURE 15:
SOLUBILITY of o-NaDBS (0% EXCESS SOLIDS) in NaCl SOLUTIONS
o-NaDBS, THIS WORK
CHANG, NaDBS (K and K Labs. Inc.) Variable % Excess Solids
0°C
0°C
-10°C
-20°C
Weight % o-NaDBS
Weight % NaCl
1.86
1.0
0.8
0.6
0.4
0.2
0.1
0.08
0.06
0.04
0.02
0.01
0.008
0.006
0.004
0.003
0
4
8
12
16
20
24

28-d

TABLE VI

SOLUBILITY OF o-NaDBS IN NaCℓ SOLUTIONS

AT VARIOUS TEMPERATURES

T°C	wt.% NaCℓ Soln.	wt.% of NaDBS in mixture	Sol.of NaDBS wt.%	wt% NaCℓ	wt.% NaDBS of mixture -excess solid phase
0	4.5	10	0.545	4.76	9.49
		8	0.470	4.63	7.55
		4	0.208	4.53	3.8
		2	0.129	4.32	1.86
		0.5	0.058	4.53	0.45
			0.026*	4.5	0
0	14.0	8	0.357	13.95	7.67
		4	0.159	13.9	3.84
		3	0.135	13.8	2.89
		2	0.098	14.09	1.91
		0.5	0.04	13.9	0.457
			0.017*	14.0	0
0	sat.salt soln.at room temp.	8	0.269	24.9	7.82
		4	0.139	23.4	3.97
		2	0.08	23.8	1.97
		0.5	0.029	25.6	0.46
			0.009*	24.0	0
-10	14.0	8	0.355	14.09	7.67
		6	0.247	14.00	5.78
		4	0.155	14.05	3.85
		3	0.131	14.10	2.87
		2	0.090	14.0	1.91
		0.5	0.037	14.05	0.46
			0.015*	14.0	0
-10	sat.salt soln.at room temp.	8	0.269	24.2	7.87
		4	0.135	23.9	3.95
		2	0.075	23.8	1.97
		0.5	0.022	24.1	0.487
			0.0072*	24.0	0
-20	sat.salt soln.at room temp.	8	0.282	22.9	7.99
		4	0.129	23.34	3.98
		2	0.073	23.37	1.97
		0.5	0.021	23.59	0.485
			0.006*	24.0	0

* Denotes extrapolated value of sol. of NaDBS at 0% excess.

Freezing waste water at low temperatures concentrates both the organic and inorganic salts simultaneously and using these solubilities at 0% excess solids, the reduction of the organic solubility by the presence of inorganics can be described quantitatively. These data show at 0°C, for example, that the solubility of o-NaDBS is markedly reduced by factors of approximately 500 in 4.5% NaCl, 800 in 14% NaCl and about 1500 in 24% NaCl. This means that if a waste water effluent containing 200 ppm NaCl and 1 ppm o-NaDBS were processed by eutectic freezing, 93% (maximum amount) of the organic would precipitate out along with the NaCl.

However, according to the observed results (see Figure 12), the solubility increases with larger amounts of solid phase in excess. Therefore, the percent of o-NaDBS that precipitates from the solution will be of a lower magnitude than 93%. Nevertheless, for the concentration of sewage in early stages, the ratio of NaCl to o-NaDBS, 200 to 1, is high. What these figures at 0% excess mean is that large amounts of organics will be preciptated before the relative NaCl concentrations become large in proportion to organic content. Furthermore, if provisions are made for continuous and immediate removal of the precipitated o-NaDBS in the purification process, the effect of the amount of excess solid phase on the solubility could be eliminated and a high degree of precipitation could be feasibly obtained. Hence, the significance of the figures at 0% excess solids becomes more important in providing useful information.

Since our data are incomplete for 0 to 4.5% NaCl solutions, the

ternary system diagram, Figure 15, is not able to be fully utilized for the process of water removal. However, if and when the nature of the data is confirmed, application of such a process to the system diagrams will follow those techniques discussed in Chapter II.

It may be observed that the NaCℓ concentration for the samples in Table VI, at 0°, -10° and -20° are at lower values than the saturated aqueous NaCℓ solutions at these same temperatures, as was expected. The solubility of NaCℓ in water, at various temperatures is given by Table VII (also see Appendix C). At -20°C, the o-NaDBS--NaCℓ--H_2O samples, made up with NaCℓ solution saturated at room temperature , are slightly more concentrated than the NaCℓ-H_2O eutectic.

TABLE VII

SOLUBILITY OF NaCℓ IN WATER (R-9)

T°C	Sol.of NaCℓ, wt.%	Solid phase(s) in equilibrium with saturated solution
+ 5	26.28	NaCℓ
+0.15 U	26.28	NaCℓ + NaCℓ·$2H_2O$
0 m	26.28	NaCℓ
0	26.26	NaCℓ·$2H_2O$
- 5	25.62	NaCℓ·$2H_2O$
-10	24.96	NaCℓ·$2H_2O$
-15	24.26	NaCℓ·$2H_2O$
-20	23.58	NaCℓ·$2H_2O$
-21.1 E	23.31	NaCℓ·$2H_2O$ + H_2O(ice)

E: Eutectic temperature

U: Transformation temperature, incongruent melting point

m: Metastable

The solubility of o-NaDBS (0% excess solids) in salt solutions over the temperature range 0° to -20°C is shown in Figure 16, in which log solubility is plotted vs reciprocal temperature. If the solutions obeyed Henry's Law, then the function R dlnS/d(1/T) is equal to the heat of solution for dissolving o-NaDBS in specific salt solutions. For the temperature range 0° to -20°C, the function for solutions of 14% NaCℓ and 24% NaCℓ is 1,325 cal/gm-mole and 2,950 cal/gm-mole, respectively.

B. Discussion of Solubility Behavior

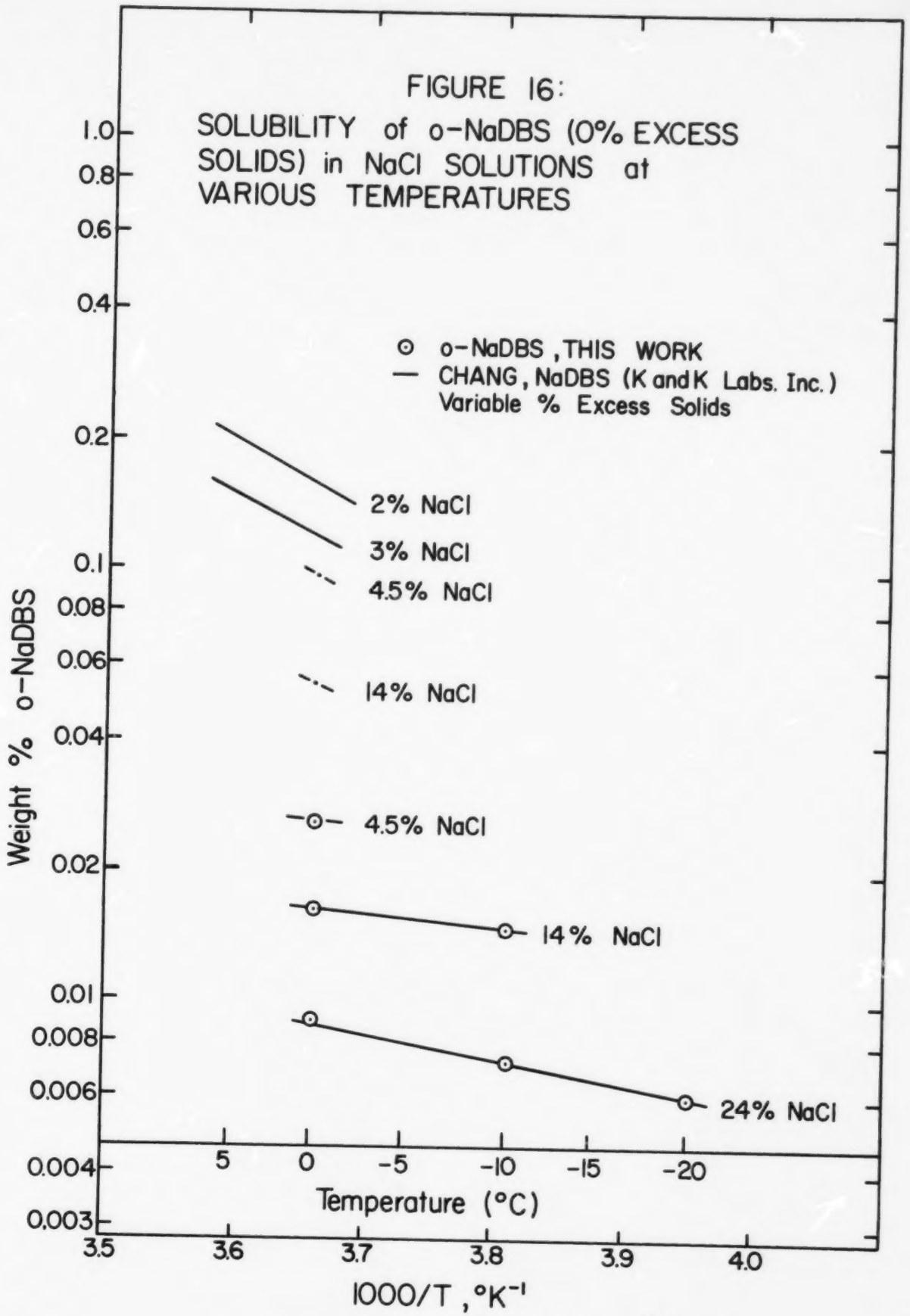
The anomalies in solubility behavior of the ortho salt, displayed by increasing solubility as the amount of excess solid phase is increased, pose a difficult problem. The cause of this abnormality may be due to hydrate formation, micelle structure, contamination of organic with water soluble impurities, equilibrium considerations (kinetic effects) or experimental error.

The formation of hydrates by members of the benzene sulfonate group of compounds has been reported in the literature. Rhodes and Lewis (R-17) reported the formation of the dihydrate of NaBS at low temperatures. Also, Renich and Taft (R-16) attributed the temperature dependence behavior of p-toluene sulfonate to hydrate formation over the temperature range of 0 - 15°C. Chang and Barduhn suggested possible hydrate formation by the NaDBS product in pure water at low temperatures.

If the hydrate were present, it would behave much like a pure component, as discussed in Chapter II--Section D3, and not affect the solubility in the manner observed during this research. The formation of a

FIGURE 16:

SOLUBILITY of o-NaDBS (0% EXCESS SOLIDS) in NaCl SOLUTIONS at VARIOUS TEMPERATURES



hydrate may take a long time to attain equilibrium, and consequently the inconsistencies in solubility could be kinetic in nature. However, after a thorough investigation of shaking times, no significant changes in the solubility results were observed. Based on the above, it was presumed that the hydrate formation would not be a primary cause of the solubility anomalies.

To establish whether or not a hydrate (or double salt) exists, a solid phase analysis, which requires the determination of the composition of excess solid phase present at equilibrium, should be performed. There was no attempt made during this study to perform such an analysis.

There is also the possibility of micelle formation or a colloidal structure in solution, which as a result would not yield a true solubility. Micelles are organic, molecular aggregates occurring in colloidal solutions. These highly charged aggregates do occur in solutions of compounds such as soap. The formation varies but it is generally a long chain of individual structural units, chemically joined to one another and positioned adjacent to each other forming bundles. It has been found that such behavior does cause some abnormalities in solubility. In 1943, Paquette et al (R-14) stated that sodium p-octylbenzene sulfonate and sodium p-dodecylbenzene sulfonate were found to be colloidal electrolytes. Also, in 1949 Shuck and Lingafelter (R-18) found that sodium Tri-isopropylbenzene sulfonate exhibited colloidal electrolyte behavior. Therefore, evidence has been found stating the fact that aqueous solutions of certain alkylbenzene sulfonates are colloidal in nature. However, it is not at all clear how the colloidal structure causes deviations from true thermodynamic solubility and in what

manner these deviations manifest themselves, especially in solutions of high ionic strength. There was no work done on this problem in the present study but the author does suggest performing electrical conductance measurements to determine if there is a colloidal structure present in the ortho salt solutions.

Of course, speculation arises as to whether equilibrium was attained in the solutions tested. As stated previously, the samples were shaken on a rocker for a period of 1 and 2 days up to 5 days. No appreciable change in the solubility of o-NaDBS in salt solutions was observed for the extended shaking periods in excess of 48 hours.

The results obtained, although abnormal in their overall character, were quite reproducible for individual saturated solution samples. As part of the routine experimental procedure to investigate experimental error, samples were taken of a particular run group, e.g. all the samples at 14% NaCℓ, two or three times at 48 hour intervals between sample removal. The percent deviation between the o-NaDBS solubilities, at -10°C, for the same solution samples of 14% NaCℓ, taken over a 3 day interval, were all less than ± 2%.

There could have been error introduced with sample preparations because of the property of o-NaDBS to absorb water from the air and the placement of NaCℓ solution in the test tubes. Also, there could have been error incurred in the preparation of the various NaCℓ solutions. The NaCℓ used was reagent grade, and was dried to drive off the excess water. However, the errors involved in the NaCℓ determinations were found to have less than ± 1% deviation. There was some error that could be attributed

to the amount of solutions titrated and their respective concentrations involved.

In summation, there was no apparent experimental error that could explain the solubility behavior observed in the experimental results. In fact, one could observe that the saturated solution samples with large excesses of solids were more yellow in color than those with relatively small amounts of solids present. Although this is just a qualitative description, it made apparent the behavior measured analytically.

The most natural thing to suspect is that there is more than one compound present, and many observers would, at first, suspect gross impurity in the ortho salt as the cause for the anomalies in solubility. The author offers the following list of analytical evidence: unequivocal synthesis, elaborate separation techniques for ortho and para separation, inorganic salt removal, conclusive identification by Infrared and UV spectral analysis. One can only suggest the possibility of an undetectable water soluble, organic impurity present in large amounts. The organic contaminant would have to possess similar physical and chemical properties to those of the ortho salt. Furthermore, it would have to be indistinguishable from the ortho salt by spectral analysis.

Presence of the p-NaDBS in any large proportions is not probable due to its relative insolubility which makes it separable through extraction procedures. Also, inspection of the IR and UV spectra for the ortho isomer reveal no peak characteristic of para isomers. On the other hand, the IR spectrum of the K & K Laboratories NaDBS product show para isomer characteristic bands and owing to their presence, these isomers are obviously

soluble. Furthermore, if the primary para isomer was present in any proportions, its very low solubility in water at low temperatures would not affect the solubility of the o-NaDBS to anywhere near the extent observed.

It was suspected that there was the possibility of homologs present in the starting material 1-phenyldodecane, with carbon lengths other than C_{12} such as C_8, C_{10}, C_{11} and C_{13} in certain percentages. Upon consultation with Distillation Products Inc., the purity (97.5% C_{12}) was determined. The carbon chain of the 1-phenyldodecane was considered to be a straight chain because the preparation reactions of the alkylbenzene rule out the possibility of a branched carbon chain. Also, upon inspection of the IR spectrum of the 1-phenyldodecane, it displayed no secondary or tertiary phenylalkane peaks. It can be assumed that no secondary or tertiary isomers are present in the starting alkylbenzene. It can, therefore, be concluded that the starting alkylbenzene, is essentially pure straight chain 1-phenyldodecane.

There is the possibility that under the circumstances involved in the sulfonation, certain side reactions occur. Gray and Krems (R-6) report the yield of the meta isomer in the synthesis used in this research is on the order of 2-3%. The yield is small mainly because the alkyl group on the benzene ring is an ortho-para director.

m-Disulfonic acids may be formed from the monosulfonic acids at high temperatures, 200-250°C, in the presence of fuming sufuric acid. Since the temperature during the course of the reaction and neutralization was always held at values less than 50°C, the disulfonic acid could not have formed to any appreciable extent.

When fuming sulfuric acid is used, sulfones, $R\text{-}SO_2\text{-}R'$, may be formed. Although, these are usually water insoluble and are removed by extraction procedures.

Rearrangement or even breakdown could occur during the reaction. However, the extent of formation of a probable, undetectable compound cannot be determined.

The author does suggest the cause of the anomalies in solubility behavior could be due to the presence of some highly water soluble organic impurity evolved through rearrangement, breakdown or possible disulfonation. It should be pointed out that the probable detergent-water structure, possibly complicated by a hydrate formation, could be the cause of the observed behavior and cannot be ignored.

These conclusions are not irrevocable or unequivocal. Further work must be conducted before a definite answer can be reached. Some specific suggestions for this work are offered in the next section.

C. Suggestions for Future Work

The author feels that there is work necessary to determine the type of solution that o-NaDBS forms in pure water. Electrical conductance measurements are suggested to investigate the probable colloidal electrolyte formation. Also, a solid phase a..alysis, such as discussed by Mader (R-11), should be conducted.

A few primary alkylbenzene sulfonates, with straight alkyl chains of carbon numbers lower than 12, could be synthesized according to the preparation used in this study. Then their respective isomeric properties investigated for comparison to the behavior of the o-NaDBS.

A more feasible alternative would be to investigate quantitatively both the solubility behavior and possible colloidal electrolyte formation of the para isomer isolated from the sulfonation of a secondary (or tertiary) phenylalkane, such as 2-phenyltridecane, which yields a high (90% or more) para distribution. A large para isomer distribution thereby reduces the degree of contamination from other isomers. Also, the UV spectra and UV absorption techniques for determination of concentration in aqueous solutions for secondary p-alkylbenzene sulfonates have been previously reported.

These secondary para isomers are more soluble than the corresponding primary para isomers and have properties similar to those of the primary ortho isomers. The solubility behavior, etc. of these para isomers could provide insight on whether the phenomena exhibited by the o-NaDBS is an individual characteristic or a property of the long straight carbon chain benzene sulfonates.

D. Conclusions

1. The o-NaDBS synthesized by the addition of oleum to 1-phenyldodecane, isolated and then identified by its IR spectrum, was much more soluble (solubility being temperature dependent) in pure water, at 0°C, than p-NaDBS and the NaDBS material used by Chang and Barduhn. Since the solubility was found to be a function of the amount of o-NaDBS solid present at saturation, the results do not represent a true thermodynamic solubility.

2. The NaCℓ greatly reduces the solubility of o-NaDBS at 0°, -10° and -20°C. The solubility of o-NaDBS in NaCℓ solutions was found to

be a function of the amount of o-NaDBS solid phase present at saturation. The o-NaDBS--NaCℓ--H_2O system was not highly temperature dependent for concentrated salt solutions over the 0° to -20°C range.

3. The o-NaDBS isomer has a characteristic UV spectrum which is quite different from the p-NaDBS spectrum. UV absorption techniques at 216 mμ were useful for the determination of o-NaDBS concentration in aqueous and NaCℓ solutions.

4. The solubility of o-NaDBS (0% excess solid phase) was obtained by extrapolation of curves (wt.% Solubility vs % excess solid phase) in various salt solutions at 0°, -10° and -20°C.

5. Further work on alkylbenzene sulfonates is required before valid conclusions can be reached concerning the solubility behavior of o-NaDBS in water and salt solutions.

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VI - APPENDICES

APPENDIX A

UV ABSORBANCE SPECTRA DATA

1. Spectrum of o-NaDBS Solution in 1 cm cell

Conc.	mμ	Absorbance	Conc.	mμ	Absorbance
50 mg/ℓ	215	1.17	50 mg/ℓ	264	0.143
aq.solvent	218	1.14		265	0.154
	220	1.05		266	0.160
	222	0.950		267	0.151
	224	0.771		268	0.142
	226	0.631		270	0.116
	230	0.351		280	0.035
	232	0.30		290	0.022
	238	0.188			
	240	0.154			
	242	0.145			
	244	0.138			
	246	0.131			
	248	0.130			
	249	0.125			
	250	0.122			
	252	0.125			
	254	0.126			
	256	0.127			
	258	0.135			
	259	0.136			
	259.5	0.142			
	260	0.139			
	262	0.139			

APPENDIX A (Cont'd.)

UV ABSORBANCE SPECTRA DATA

2. Spectrum of p-NaDBS Solution in 1 cm cell

Conc.	mμ	Absorbance
.3 gm/ℓ	214.5	1.28
aq.solvent	215	1.30
	217	
(300 mg/ℓ)	220	1.67
	223	1.69
	224	1.63
	226	1.6
	230	1.1
	240	0.130
	250	0.125
	260	0.125
	270	0.092
12 mg/ℓ	215	0.087
aq.solvent	218	0.102
	220	0.110
	222	0.114
	223	0.117
	224	0.114
	225	0.109
	230	0.07
	240	0.003
	250	0.003
	260	0.004
	270	0.004

APPENDIX B

SAMPLE DATA SHEET AND SOLUBILITY CALCULATIONS

Name: J. N. Cesaro Date: 6/25/65

Subject: Solubility of o-NaDBS-NaCℓ-H_2O: -10°C

RUN NO.	EP-EHA-$\overline{10}$-14-1	EP-EHA-$\overline{10}$-14-2	EP-EHA-$\overline{10}$-14-3
Flask(gms.)	55.4088	47.8173	57.1175
Flask + Sample(gms.)	56.1208	48.4120	57.4979
Sample(gms.)	0.7120	0.5947	0.3804
Dilution	--- to	100 cc	---
Vol.of 100 cc Titrated(cc.)	20	20	20
Vol.of.1N $AgNO_3$	3.4	2.86	1.84
Wt.% NaCℓ in sat. soln.	14.0	14.05	14.09
gms.NaCℓ/ℓ	0.99	0.83	0.54
A/A_o corr.for NaCℓ	0.004	0.004	0.004
A/A_o(uncorr.)	0.175	0.247	0.365
A/A_o(corr.)	0.171	0.243	0.361
mg/ℓ	6.4	9.2	13.8
Wt.% DBS in sat.soln.	0.09	0.155	0.355
Wt.% DBS in total mixture	2.0	4.0	8.0

Calculations for EP-EHA-$\overline{10}$-14-1

a) Wt.% NaCℓ

$$V_{C\ell}N_{C\ell} = V_{Ag}N_{Ag}$$

$$N_{C\ell} = \frac{V_{Ag}N_{Ag}}{V_{C\ell}}$$

$$\frac{N_{C\ell}}{\text{Sample Wt.(gm/100 cc)}} \left| \frac{58.45 \text{ gms. NaC}\ell/\ell}{N} \right| 0.1\ \ell/100\text{ cc} \left| 10^2 \right. = \text{wt.\% C}\ell$$

$$\frac{V_{Ag}N_{Ag}}{V_{C\ell}} \left| 58.45 \right| \frac{}{\text{Sample weight}} \left| 0.1\ \ell/100\text{ cc} \right| 10^2 = \text{wt.\% C}\ell$$

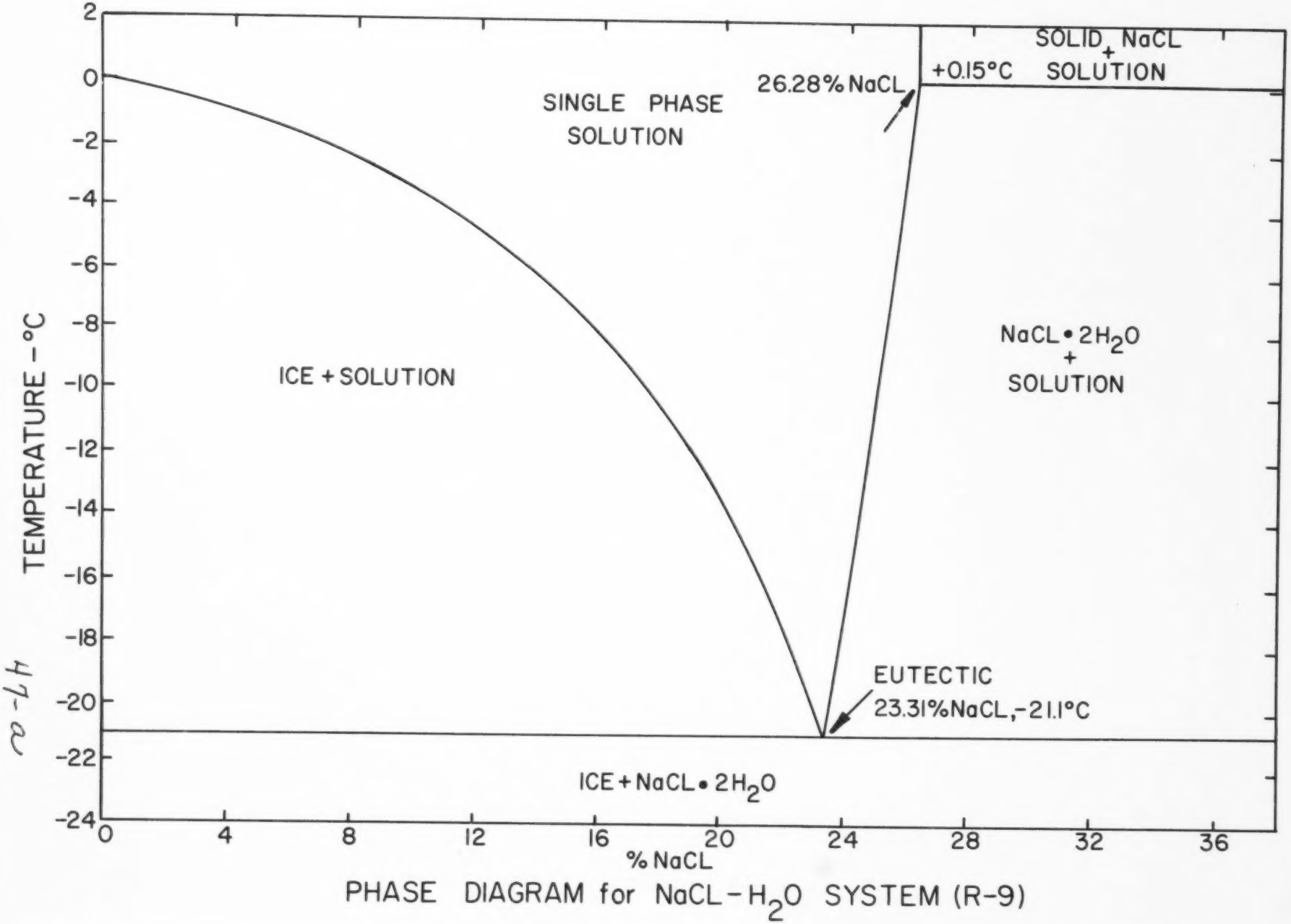
$$\frac{3.4}{20} \left| 0.1 \right| \frac{58.45}{0.7120} \left| 0.1 \right| 10^2 = \underline{14.0\%}$$

b) Wt.% NaDBS

$$\frac{6.4 \text{ mg}}{\ell} \left| \frac{10^{-4} \text{ gm}/100 \text{ cc}}{\ell} \right| \frac{}{0.7120 \frac{\text{gm}}{100 \text{ cc}}} \left| 10^2 \right. = \underline{0.09\%}$$

APPENDIX C

$NaCl-H_2O$ Phase Diagram



PHASE DIAGRAM for NaCL - H_2O SYSTEM (R-9)

$NaCl$-H_2O PHASE DIAGRAM DATA (R-9)

T°C	M ± 0.2%	M x 58.45	M x 58.45 + 1000	wt.% NaCl
	S · 2AQ + Ice			
-21.1E	5.20	303.94	1303.94	23.31
	S · 2AQ			
-20	5.28	308.62	1308.62	23.58
-15	5.48	320.31	1320.31	24.26
-10	5.69	332.58	1332.58	24.96
- 5	5.90	344.85	1344.85	25.62
	S · 2AQ + S			
+ 0.15U	6.10	356.55	1356.55	26.28
S				
0m	6.10	356.55	1356.55	26.28
5	6.10	356.55	1356.55	26.28
10	6.11	357.13	1357.13	26.32
15	6.12	357.71	1357.71	26.35
20	6.13	358.30	1358.30	26.39

S: anhydrous NaCl

M: gm-formula wt./1000 gm H_2O

E: eutectic temperature

U: transformation temperature, incongruent melting point

m: value in metastable region